Advanced characterization of passivation layers in perovskite solar cells via GIWAXS

Organic–inorganic perovskite solar cells (PSCs) are highly anticipated as next-generation photovoltaic devices owing to their high efficiency and ease of fabrication. These devices can be conveniently fabricated using a solution-based process, which is generally followed by thermal treatment [1]. However, the A-site cations in halide perovskite crystals (ABX_3) include organic cations, making them susceptible to the formation of cation vacancies due to external factors such as heat and light. Additionally, halide perovskite crystals contain halide anions such as iodide (I^-), which is particularly prone to oxidation. Upon photoirradiation, iodide vacancies tend to form, leading to the generation of defects on the perovskite crystal surface during thermal treatment. The formation of these ion vacancies facilitates ion migration, which has been reported to be a critical factor affecting device durability. Theoretical calculations indicate that halide ions are the predominant migrating species, and the presence of methylammonium (MA) vacancies (V'_{MA}) enhances iodide ion (I^-) migration. An increase in the V'_{MA} concentration has been correlated with a higher ionic conductivity for I^-. Furthermore, detached iodide ions migrate within the perovskite crystal and device, leading to electrode corrosion and perovskite degradation, and thereby significantly reducing device longevity.

The introduction of passivation layers has been investigated to mitigate ion vacancies and suppress ion migration. A promising approach involves the formation of low-dimensional perovskite structures to compensate for the defects in halide perovskite crystals. Two-dimensional perovskites incorporating organic halide compounds such as PEAX (X = I, Br, and Cl) have been found to be effective. Additionally, nonreactive organic polymers such as polyetherimide, which do not interact with perovskite crystals, have also demonstrated beneficial effects. Thus, compensating for surface defects in halide perovskite crystals using these methods may effectively enhance the device stability. However, commonly reported passivation materials generally exhibit low conductivity, necessitating the formation of ultrathin films on the order of a few nanometers. Achieving precise control over such thin-film deposition via solution processes remains a significant challenge.

We used gallium hydroxide phthalocyanine (OHGaPc, Fig. 1(a)) as a passivation layer [2]. Unlike conventional insulating passivation materials, OHGaPc is a crystalline p-type organic semiconductor that facilitates charge transport. Additionally, its hydroxyl functional groups allow it to compensate for defects on the outermost surface of the perovskite crystals. Because of these properties, OHGaPc is expected to function as both a charge-transport material and passivation layer. Grazing incidence wide-angle X-ray scattering (GIWAXS) was used to examine the structural characteristics of the OHGaPc films on the perovskite layers. Two-dimensional GIWAXS patterns represented in reciprocal space were obtained at SPring-8 **BL19B2**. The samples were irradiated with X-rays of 12.39 keV (λ = 1 Å) at a fixed incident angle of 0.12°. GIWAXS measurements of the OHGaPc films deposited on the perovskite thin layers are shown in Figs. 2(a,b). The observed diffraction pattern resembles that of OHGaPc on a Si substrate, suggesting a similar molecular packing arrangement. The crystal structure of OHGaPc has been identified as triclinic (P-1), with the following lattice constants: $a = 11.52$ Å, $b = 12.75$ Å, $c = 8.89$ Å, $\alpha = 95.87°$, $\beta = 96.00°$, and $\gamma = 69.45°$ [3]. The diffraction signal corresponding to the (010) crystal plane derived from these structural parameters aligned with the peak observed in the q_z axis direction. Additionally, the azimuthal angle ($90° - \gamma$) and position of the (100) diffraction peak (located at an azimuthal angle of 20°) supported the conclusion that the OHGaPc polycrystalline film primarily adopted a (010) preferred orientation. As depicted in Fig. 2(c), two distinct π–π stacking arrangements were observed. The first configuration exhibited an intermolecular centroid separation of 3.690 Å and offset distance of 1.173 Å, while the second structure had a centroid separation of 3.895 Å and an offset distance of 1.253 Å. Because these π–π stacking distances were less than 4 Å, they indicated the possibility of effective charge transport pathways. However, because of the predominant in-plane alignment of the π–π stacking direction, charge mobility along the stacking axis may have been constrained. Thus, tuning the molecular orientation

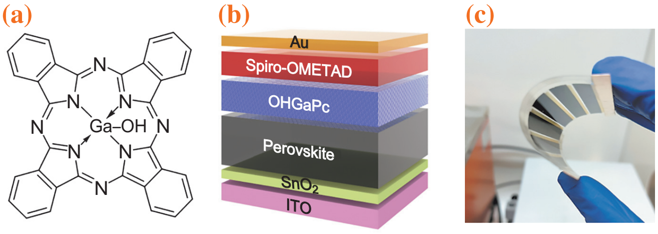

Fig. 1. **(a)** Chemical structure of OHGaPc. **(b)** Structure of perovskite solar cell. **(c)** Flexible perovskite solar cell.

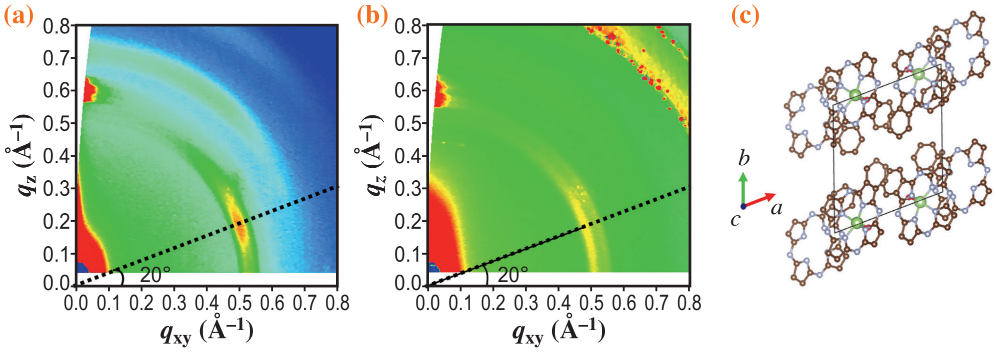

Fig. 2. GIWAXS patterns of OHGaPc thin films on **(a)** PVK and **(b)** Si, along with **(c)** detailed crystal structure of OHGaPc.

could be a key factor in optimizing the charge-transport properties.

To evaluate the impact of OHGaPc on the device durability, PSCs incorporating an OHGaPc interlayer were fabricated. The device structure was [ITO/SnO_2/perovskite/OHGaPc/spiro-OMeTAD/Au] (Fig. 1(b)). The highest power conversion efficiency (PCE) achieved for PSCs with OHGaPc was 21.0%. In contrast, the best PCE obtained for the PSCs without the OHGaPc interlayer was 21.8%. Although the introduction of OHGaPc resulted in a slight reduction in PCE, this decrease was attributed to an increase in the series resistance. Generally, the thickness of the passivation layer is on the order of a few atomic layers. However, in this study, despite the OHGaPc film reaching a thickness of several tens of nanometers, only a minor increase in the resistance was observed, demonstrating its high charge-transport capability. In addition, durability tests of the PSCs incorporating OHGaPc were conducted to evaluate their photostability. Their improved stability was attributed to the suppression of ion migration, which was analyzed using time-of-flight secondary-ion mass spectrometry (TOF-SIMS). The extent of ion migration was assessed by examining the ion distribution along the film stacking direction (Fig. 3). A significant increase in I^- and Br^- ion intensity was observed within the hole transport layer (HTL) in samples without OHGaPc, indicating substantial ion migration during the photostability test. In contrast, no increase in I^- and Br^- intensity was detected within the HTL in samples containing OHGaPc, demonstrating that the OHGaPc interlayer effectively blocked ion migration. These findings suggested that the incorporation of OHGaPc suppressed ion migration and significantly enhanced the photostability of the device.

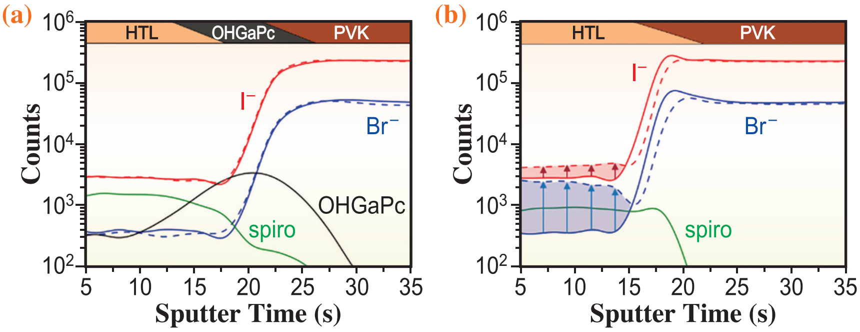

Fig. 3. Depth profiles of ions in perovskite solar cells measured using TOF-SIMS: **(a)** with and **(b)** without OHGaPc.

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