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A synergistic effect of the ion beam sputtered NiO_x hole transport layer and MXene doping on inverted perovskite solar cells

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During the past few years, organic-inorganic halide perovskite solar cells (PSCs) have gained attention owing to a

Abstract

The synergistic effect of high-quality NiO_x hole transport layers (HTLs) deposited by ion beam sputtering on ITO substrates and the Ti₃C₂T, MXene doping of CH₃NH₃PbI₃ (MAPI) perovskite layers is investigated in order to improve the power conversion efficiency (PCE) of p-i-n perovskite solar cells (PSCs). The 18 nm thick NiO_x layers are pinhole-free and exhibit largescale homogeneous surface morphology as revealed by the atomic force microscopy (AFM). The grazing-incidence x-ray diffraction showed a 0.75% expansion of the face-centered cubic lattice, suggesting an excess of oxygen as is typical for non-stoichiometric NiOx. The HTLs were used to fabricate the PSCs with MXene-doped MAPI layers. A PSC with undoped MAPI layer served as a control. The size of MAPI polycrystalline grains increased from 430 ± 80 nm to 620 ± 190 nm on the doping, as revealed by AFM. The 0.15 wt% MXene doping showed a 14.3% enhancement in PCE as compared to the PSC with undoped MAPI. The energy-resolved electrochemical impedance spectroscopy revealed one order of magnitude higher density of defect states in the band gap of MXene-doped MAPI layer, which eliminated beneficial effect of reduced total area of larger MAPI grain boundaries, decreasing short-circuit current. The PCE improvement is attributed to a decrease of the work function from -5.26 eV to -5.32 eV on the MXene doping, which increased open-circuit voltage and fill factor.

Keywords: ion beam sputtering, NiO_x hole transport layer, MXene, power conversion efficiency, perovskite solar cells

(Some figures may appear in colour only in the online journal)

1. Introduction

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rapid increase in the power conversion efficiency (PCE) from 3.8% up to 25.8% recently [1]. In PSCs, the perovskite layer is sandwiched between an electron transport layer (ETL) and a hole transport layer (HTL) [2, 3]. Inorganic HTLs have been extensively studied due to their high charge mobility and environmental stability. In particular, NiO_x has attracted a lot of attention owing to its large band gap and deep-lying valence band. This renders it a favorable candidate for efficient charge extraction due to its better band alignment with the halide perovskite absorber [4]. The NiO_x HTLs can be prepared by various methods such as the spin coating of NiO_x colloids [5], thermal evaporation [6], magnetron sputtering [7], and pulsed laser deposition [8, 9]. Research into the scaling up of these deposition methods is needed to develop efficient large-area NiO_x-based PSCs.

In addition to HTL, the quality of the perovskite absorber layer also plays a vital role in the device performance. Although a lot of research has been carried out to improve the properties of perovskite layer, there is still room for its improvement in terms of enhancing the quality of crystal structure, reducing the density of trap states, increasing the grain size, and improving the quality of perovskite interfaces with the charge selective layers [10]. Therefore, the introduction of new materials into the perovskite layer can be a beneficial strategy to boost the properties of the perovskite absorber layer. In particular, MXenes have been recently employed to enhance PSC performance. MXenes are twodimensional (2D) materials with general notation $M_{n+1}X_nT_x$, where M is an early transition metal, X denotes carbon and/or nitrogen, and T_x represents the surface termination functional groups (O, OH, F) [11, 12]. The rich chemistry of surfacetermination groups makes MXenes a suitable candidate with many options for tuning their electronic properties. The studies in this direction have started on PSCs with n-i-p architecture. Agresti et al improved PCE of PSC by 26% by tuning the work function of the absorber layer and interfacial engineering with MXene [13]. Wang et al reduced the trap state density by employing an MXene-modulated electrode/SnO₂ interface as a platform for the perovskite film growth [14]. Guo et al used MXenes as additive in the perovskite layer, retarding the crystallization rate and reducing the number of grain boundaries, thus enhancing the PCE [15]. Later on, Saranin et al modified the work function and band alignment in the p-i-n PSCs with solution-processed NiO_x HTL by MXene doping of the photoactive perovskite layer and/or ETL, achieving 19.2% PCE [16]. In addition to the energy level alignment, passivation of the trap states within the device and improved charge collection/extraction at the electrodes contributed to the PCE enhancement.

In this work, we prepared high-quality NiO_x layers with a thickness of 18 nm by the ion beam sputtering (IBS) method with tightly controlled deposition parameters. These NiO_x layers were employed as HTLs in PSCs with $Ti_3C_2T_x$ MXene-doped CH₃NH₃PbI₃ (MAPI) perovskite layers. The MXene effect on its photovoltaic performance was investigated. Unlike previous studies, where the $Ti_3C_2T_x$ MXene-doping of MAPI was at the level of 0.03 wt% [15] or even less [16], which resulted in a 12% or 8.6% PCE improvement,

ence was that our MXene sheets were not delaminated down to few monolayers and their lateral size was approaching the thickness of the absorber layer. The MAPI layer doped with 0.15 wt% of such MXene improved PCE by up to 14.3% compared to the undoped PSC, increasing both $V_{\rm OC}$ and FF, which is more than in previous studies. This demonstrates potential of MXenes as the dopant of the perovskite absorber to boost performance of PSCs with the p-i-n architecture and IBS deposited HTL.

we examined a higher doping concentration. Another differ-

2. Experimental section

2.1. Preparation of NiO_x layers by the ion beam sputtering

Prior to the deposition of NiO_x layers on ITO substrates, the substrates were cleaned using a standard process applied for PSCs fabrication. The clean substrates were placed in an IBS vacuum chamber (Bestec, Germany) with a base pressure of $(1-3) \times 10^{-8}$ mbar and were annealed at 120 °C for 1 h to desorb potential contaminants. The Ni target was pre-sputtered by pure Ar gas for 20 min to remove oxide layer and impurities from previous depositions. A mixture of Ar and O₂ at Ar: $O_2 = 5:1$ flow rate ratio was used for the NiO_x sputtering, resulting in a working pressure of 6.4×10^{-4} mbar. The ion source was operated with a RF power of 65 W, the total ion current and accelerating voltage being 23 mA and 600 V, respectively. The deposition was done at room temperature for 30 min at a rate of 0.08–0.1 Å s⁻¹. After deposition, the NiO_x layer was annealed at 250 $^{\circ}$ C for 30 min and then at 300 °C for 5 min in air.

2.2. PSCs device fabrication

The details of the fabrication of PSCs are described elsewhere [17]. For the preparation of the MXene-doped MAPI layer, 1.45 M of MAPI was mixed with 0.15 wt% of delaminated MXene powder ($Ti_3C_2T_x$, Nanochemazone, Canada) and sonicated for 15 min before deposition. Next, the MAPI/ MXene solution was spin-coated on NiO_x HTL by a two-step process (1000 rpm for 10 s followed by 5000 rpm for 45 s). 5 s after the second step, 0.2 ml of chlorobenzene was dropped on the MAPI/MXene layer to initiate the perovskite crystallization. Subsequently, the samples were annealed in the dark at 50 °C for 2 min and then at 100 °C for 20 min inside a glovebox. Afterwards, PC₆₁BM and BCP layers were deposited by spin-coating [17]. Finally, a 125 nm thick Ag layer as conductive electrode was evaporated in a chamber interlocked with the glovebox. The undoped and MXenedoped MAPI layers on ITO substrate with PEDOT:PSS HTL were prepared separately to examine the effect of the doping on the density of states. The MAPI films were characterized in ambient atmosphere at a temperature of 25 °C and humidity of $\sim 30\%$.



Figure 1. (a) PSC design. (b) AFM image and (c) GIXRD pattern of the NiO_x layer on ITO. (d) Transmittance spectra of bare ITO and the NiO_x layer on ITO.

2.3. Characterization and measurements

A recently developed energy-resolved electrochemical impedance spectroscopy (ER-EIS) was employed to obtain the density of states (DOS) in the layers of NiO_x and MAPI. A detailed description of the experiment can be found elsewhere [18, 19]. Atomic force microscopy (AFM) images were measured in the tapping imaging mode (Dimension Edge Bruker, Germany). Optical absorption was measured using an UV–vis–NIR spectrophotometer (SolidSpec–3700 Shimadzu, Japan). The *J–V* curves and external quantum efficiency (EQE) were measured by a standard equipment for measuring solar cells (ReRa Solutions, The Netherlands). The formation of the NiO_x layer on ITO substrate was checked by the x-ray diffraction at grazing incidence (GIXRD, Discover 8 Bruker, Germany).



Figure 2. DOS function of IBS NiO_x and undoped MAPI layers obtained with ER-EIS.

3. Results and discussion

A schematic view of the PSCs under study is shown in figure 1(a). The AFM surface topography of the NiO_x layer prepared by ion beam sputtering on ITO substrate is shown in figure 1(b). The NiO_x layer exhibits a homogeneous, pinhole-free morphology with a RMS roughness of 4.2 nm. A GIXRD pattern of the NiO_x layer measured at 0.2° grazing angle

(figure 1(c)) exhibits 3 diffraction peaks, which are shifted to lower angles with respect to the stoichiometric NiO phase with face-centered cubic (fcc) lattice. This suggests an expansion of the cubic lattice parameter by 0.75% due to the excess of oxygen as it is typical for the non-stoichiometric NiO_x phase. This slight deviation from NiO stoichiometry improves performance of HTL and can easily be adjusted by IBS unlike other preparation methods. Some ITO diffractions



Figure 3. (a) Delaminated MXene sheets. AFM images of (b) undoped and (c) MXene-doped MAPI layers. The grain size distributions of (d) undoped and (e) MXene-doped MAPI layers calculated from AFM images. (f) Measured optical absorbance.

coming from the substrate are visible as well. The optical transmittances of the bare ITO substrate and the NiO_x layer on ITO (figure 1(d)) show that NiO_x does not significantly compromise the optical transmittance in the visible region compared to bare ITO, as is required for the PSCs with HTL on the front side. The DOS of NiO_x and MAPI layers are depicted in figure 2. The ER-EIS shows two orders of magnitude lower DOS of the NiO_x compared to the DOS of the MAPI layer in the conduction band ($E \approx -3.5 \text{ eV}$), which confirms the blocking nature of NiO_x and MAPI in the valence band ($E \approx -6 \text{ eV}$) match well each other, which is important for efficient drain of generated holes.

A SEM image of the delaminated multilayer MXene sheets is shown in figure 3(a). The AFM images of the MAPI and MXene-doped MAPI layers are shown in figures 3(b) and (c), respectively. Both layers are spatially uniform and have no apparent pinholes that would adversely affect the optoelectronic properties. Still more importantly, the MXene doping results in an increased grain size of MAPI and thus reduces the total area of grain boundaries. The grain size distributions in the MAPI (figure 3(d)) and MXene-doped MAPI (figure 3(e)) layers calculated from AFM show that the average grain size of MAPI grows from $430 \pm 80 \text{ nm}$ to $620 \pm 190 \,\mathrm{nm}$ due to the MXene doping. The grain size distributions were obtained using the ImageJ analyzing software by manual tracing the individual grain boundaries, which provides the grain volume and lateral dimensions. The increase of the MAPI grain size due to the MXene doping can be attributed to the negatively charged surface termination groups of MXene sheets, which bind to MA cations and slow down MAPI crystallization [15, 20]. The doping also increases the optical absorbance (figure 3(f)) due to the higher light absorption by MXene sheets. This is not surprising as it can be seen from figure 3(a) that these sheets are not few-layer MXene nanosheets, which are almost completely transparent, but larger and much thicker multilayer sheets.

To investigate the effect of MXene doping on the performance of PSCs, complete PSC devices were fabricated employing the above described NiO_x layer as HTL and either MAPI or MXene-doped MAPI as the photoconversion layer. The *J*–*V* curves and external quantum efficiencies (EQE) of the best devices are shown in figures 4(a) and (b), respectively, while the statistical information on the photovoltaic parameters is shown in figure 5. The best devices with identical 18 nm thick NiO_x HTL exhibited PCE of 14% and 16% for the undoped and doped devices, respectively, which represents a 14.3% improvement. A 10% PCE improvement was found after averaging on 12 devices, which is comparable with previous studies [15, 16].

Comparing the *J*–*V* curves and statistics of photovoltaic parameters of the undoped and MXene-doped PSCs, we can see that MXene doping has a major impact on V_{oc} and FF rather than on J_{sc} . This can be explained by the observed decrease of the work function of MAPI layer from -5.26 eVto -5.32 eV on the MXene doping. A similar decrease was observed previously [16]. It can also be seen that the MXene doping of MAPI preserves a nearly wavelength-independent behavior of EQE (figure 4(b)). This suggests that despite increasing the optical absorbance (figure 3(f)), the MXene sheets are not actively involved in the photogeneration of charge carriers, confirming that their beneficial effect is solely



Figure 4. The best undoped and MXene-doped MAPI devices (a) J-V curves (b) external quantum efficiencies.



Figure 5. Statistics of photovoltaic parameters of the undoped and MXene-doped MAPI devices (reverse scan).

connected with enhancing MAPI crystallization, as emphasized earlier [15]. Larger MAPI grains and fewer grain boundaries on the doping result in the reduced total boundary area, which should suppress non-radiative recombination at trap states typically formed at grain boundaries [21], improving PSC parameters [22]. However, even MXene's excellent conductivity is not reflected in the better J_{sc} . Presumably, the large and thick multilayer MXene sheets (figure 3(a)) are likely to extend up to the MAPI/ETL interfaces and create a number of trap states, which are typically formed at the interfaces of the MAPI layer with the charge extracting layers. Indeed, the ER-EIS measurements revealed an order of magnitude higher density of defect states in the band gap as well as the band of shallow states below the conduction band due to the MXene doping of the MAPI layer (figure 6). In particular, the deep defect states close to the center of band gap promote recombination and suppress $J_{\rm sc}$. Aggregates of MXene sheets on the surface of the MAPI layer, which may act as the carrier recombination centers [23], have also been observed in the past [15].

The hysteresis index of the undoped device calculated from the J-V curve was found to be 5.5%, while the doped



Figure 6. DOS function of the undoped and MXene-doped MAPI layers obtained with ER-EIS.

devices exhibited greater hysteresis (up to 12%). For PSCs, the ion movement-mediated migration of charged halide defects (vacancies, interstitials) in an applied electric field is assumed as the most probable origin of the observed hysteresis [24]. According to Azpiroz et al [25], the migration of MA and Pb vacancies with calculated activation barriers of \sim 0.5 and 0.8 eV, respectively, results in the migration time in the range of seconds or minutes, which is comparable with the hysteresis process time. Increased activation energy of migration was observed for perovskite layer with larger grains in comparison to that with smaller ones [26]. Given these facts, a 44% larger perovskite grain size in the MXene doped MAPI device may contribute to increased hysteresis through increased activation energy of defect migration, but cannot explain the entire 118% increase. Therefore, the increase in hysteresis can be attributed in particular to the distinct increase of the number of defects in the MAPI layer initiated by MXene doping, as can be seen from the increased density of defect states in the band gap in figure 6. Hence, similar to the decrease in J_{sc} after doping with MXene, the greater hysteresis of the doped devices can be explained by the increased defect formation in the MAPI layer. The large and partly delaminated multilayer MXene sheets increasing the DOS in band gap are the main reason of different results compared to the previous PSC study with NiO_x HTL [16]. Yet, we achieved larger PCE improvement, which demonstrates potential of MXenes for PSCs. Systematic optimization of MXene concentration in the future holds promise to further improve PCE. The employment of multilayer MXene sheets produced by the less expensive and faster delamination process, which proved to be fully sufficient, is the added value of our approach.

4. Conclusion

We investigated the synergistic effect of high-quality NiO_x HTL layers prepared by IBS method and $Ti_3C_2T_x$ MXene doping of MAPI perovskite layers on the performance of PSCs. The MXene sheets enhance perovskite crystallization, leading to larger crystalline grains and reduced total area of grain boundaries, which should decrease non-radiative recombination. However, MXene doping causes an increase in the number of defect states in the band gap of MAPI, eliminating the beneficial effect of larger grains. Therefore, the increase in V_{OC} and FF due to MXene doping is attributed to the measured decrease of the work function of MAPI. As a result, a maximum 14.3% and average 10% improvement in PCE was achieved for the PSCs with the 0.15 wt% MXenedoped MAPI layers. Partly delaminated multilayer MXene sheets were sufficient, suggesting possible cost and time savings in upscaling the fabrication. These results have direct implications for boosting the performance of the inverted PSCs with p-i-n architecture via high-quality IBS deposited HTLs and MXene doping of the perovskite layer.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Notes

The authors declare no competing financial interest.

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