Polysilane-Inserted Methylammonium Lead Iodide Perovskite Solar Cells Doped with Formamidinium and Potassium

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Abstract: Polysilane-inserted CH$_3$NH$_3$PbI$_3$ perovskite photovoltaic devices combined with potassium and formamidinium iodides were fabricated and characterized. Decaphenylcyclopentasilane layers were inserted at the perovskite/hole transport interface and annealed across a temperature range of 180–220 °C. These polysilane-coated cells prevented PbI$_2$ formation, and the conversion efficiencies were improved over extended periods of time.

Keywords: polysilane; decaphenylcyclopentasilane; perovskite; photovoltaic device; solar cell; formamidinium; potassium

1. Introduction

Although the most commonly used solar cells are currently silicon-based, these silicon devices have a complicated fabrication process, and the silicon semiconductor has an indirect transition band structure. Since recently developed CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$)-based perovskite compounds have demonstrated numerous advantages, such as direct bandgaps, easy fabrication process, and high conversion efficiencies [1–4], these compounds are considered as major candidates for next-generation solar cell materials. However, lead halide compounds are typically unstable in air; thus, the stability of the corresponding perovskite photovoltaic devices should be improved for inclusion in the actual cell module [5,6]. The instability of the perovskite photovoltaic devices results from the migration of CH$_3$NH$_3$ (MA) and reactivity with H$_2$O [7,8].

To improve the stability of the perovskite photovoltaic devices, polymeric materials have been investigated [9–14]. For instance, poly(methyl methacrylate) and poly(propylene carbonate) have been used to protect the perovskite layer from oxygen and moisture [15,16] and to enhance stability. Both polymeric materials formed cross-linked networks comprising perovskite grains, which suppressed defects. Furthermore, the stability was also influenced by hole transport layers (HTLs) [17]. In practice, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) is widely applied as a HTL for perovskite photovoltaic devices; however, this material is expensive, and the electronic properties degrade at elevated air temperatures. Alternative hole transport materials have been reported [18,19], and polysilane derivatives have also been investigated [20].

Polysilane derivatives exhibit two important advantages. The first relates to polysilanes being $p$-type semiconductors that facilitate hole transfer and rectification at the $p$-$n$ junction [20]. The second
where \( r \) is the ionic radius of the A, B, and X ions. When \( t \) is close to 1, the perovskite structure is expected to be more structurally stable, although the ionic properties are not considered.

The tolerance factor of MAPbI\(_3\) is calculated to be 0.912 [27], and this indicates that MAPbI\(_3\) may be slightly unstable. To increase the \( t \)-factor and reduce the migration of MA, formamidinium (FA: \( \text{CH}_3(\text{NH}_2)_2 \)) with a larger ionic radius (2.53 Å) than MA (2.17 Å) was doped at the MA site, and the stabilities of the perovskite solar cells were improved by FA addition [31–33]. Studies on devices with ethylammonium (EA: \( \text{CH}_3\text{CH}_2\text{NH}_3 \)) [34,35] or guanidinium (GA: \( \text{C}(\text{NH}_2)_3 \)) [36,37] addition to perovskites have also been reported.

Since the above MA, FA, EA, and GA are molecules, they may affect the stabilities of the perovskite crystals. Therefore, substitution of alkali metal elements such as cesium (Cs), rubidium (Rb), potassium (K), and sodium (Na) might be effective in avoiding the migration and desorption of A-site elements in the perovskite crystals. It is also expected that the semiconductor characteristics of the perovskite crystals can be controlled by alkali element doping. Effects of Na and K doping to MAPbI\(_3\) crystals on the electronic structures were investigated by first-principles calculation [42]. Partial substitution of MA with Na or K generated electronic orbitals of Na or K above the conduction band, which would facilitate charge transfer from the alkali metals to the conduction band. This may then accelerate carrier diffusion related to the photovoltaic performances. Conversion efficiencies and stabilities were reported to be improved by adding Cs\(^+\) and Rb\(^+\) to perovskite precursor solutions, which increased grain sizes and reduced defect densities [43–46]. Conversion efficiencies were also improved by using K, which offers a lower cost than Rb and Cs. A calculated \( t \)-factor of K doping alone to MAPbI\(_3\) indicates that the structural stability of perovskite compounds was reduced [27], and other cations with larger cationic radii, such as FA and EA, may be necessary to form more stable perovskite structures.

Herein, the focus is to investigate the photovoltaic properties and stabilities of DPPS-inserted MAPbI\(_3\) perovskite solar cells doped with potassium (K) and formamidinium (FA), which are denoted as MA(FA,K)PbI\(_3\). Previously, co-addition of K and FA was reported to be effective for enhancing the photovoltaic properties [47–51]. In the present work, the MA(FA,K)PbI\(_3\) perovskite compounds, prepared at temperatures in the range of 180–220 °C in ambient air, were evaluated in terms of the
photovoltaic properties and stability. The effects of annealing temperatures and polysilane addition on the microstructures and photovoltaic properties of the MA(FA, K)PbI₃ perovskite solar cells were investigated using current density voltage (J-V) characteristics and X-ray diffraction (XRD).

2. Materials and Methods

A fabrication process of the present solar cell devices is schematically illustrated in Figure 1. The fabrication conditions were ~27 °C temperature and ~40% humidity in ambient air [52,53]. F-doped tin oxide (FTO, Nippon Sheet Glass Company, Tokyo, Japan, ~10 Ω/cm²) substrates were cleaned by methanol and acetone in an ultrasonic bath and an ultraviolet ozone cleaner (Asumi Giken, Tokyo, Japan, ASM401N) [26,54]. Next, 0.15 and 0.30 M precursor solutions of TiO₂ compact layers were prepared from 1-butanol (Wako Pure Chemical Industries, Osaka, Japan) and titanium disopropoxide bis(acetylacetonate) (Sigma Aldrich, Tokyo, Japan). These precursor solutions of compact TiO₂ were spin-coated on the FTO substrate at 3000 rpm for 30 s, and the substrates were annealed at 125 °C for 5 min. To form a uniform compact TiO₂ layer, the 0.30 M precursor solution was spin-coated twice. Then, the FTO substrate was annealed at 550 °C for 30 min to form the compact TiO₂ layer. After that, a TiO₂ paste (precursor solution for mesoporous TiO₂) was spin-coated on the compact TiO₂ layer at 5000 rpm for 30 s. This TiO₂ paste was prepared by mixing distilled water (0.5 mL), poly(ethylene glycol) PEG-20000 (Nacalai Tesque, Kyoto, Japan, PEG #20000, 20 mg), and TiO₂ powder (Aerosil, Tokyo, Japan, P-25, 200 mg). This solution was further mixed with the surfactant Triton X-100 (Sigma Aldrich, 10 µL) and acetylacetone (Wako Pure Chemical Industries, 20 µL) for 30 min, and it was left untouched for 24 h to remove bubbles in the solution [53]. To form the mesoporous TiO₂ layer, the TiO₂-coated substrates were annealed at 550 °C for 30 min.

![Figure 1. Schematic illustration detailing the processes adopted to fabricate the perovskite photovoltaic devices and a photograph of the device.](image)

The perovskite compounds were prepared by mixing N,N-dimethylformamide (DMF; Sigma Aldrich) solutions of KI (Wako Pure Chemical Industries), HC(NH₂)₂I (Tokyo Chemical Industry, Tokyo, Japan), CH₃NH₃I (Tokyo Chemical Industry), and PbCl₂ (Sigma Aldrich) at 60 °C for 1 day. The basic precursor of MAPbI₃ was prepared with molar concentrations of PbCl₂ and MAI of 0.8 and 2.4 M, respectively [53,55], and MA₀.₆₄FA₀.₃₁K₀.₀₅PbI₃ and MA₀.₄₈FA₀.₄₇K₀.₀₅PbI₃ precursors were prepared by adding FAI and KI to control the desired molar ratio. As the FA composition increased, the tolerance factor (t-factor) increased toward 1 [27], which indicated the crystal distortion in the perovskite structure could be reduced by FA addition. Perovskite precursor solutions were spin-coated on the mesoporous TiO₂ layer three times. For the first spin-coating, the perovskite solutions were spin-coated at 2000 rpm for 60 s. During the second and third spin-coatings, a hot air-blowing method was applied [27]. Temperatures of the cells during the air-blowing were set at 90 °C. A polysilane solution was prepared by mixing chlorobenzene (Fujifilm Wako Pure Chemical Corporation, 0.5 mL) with DPPS (Osaka Gas Chemicals, Osaka, Japan, OGSOL SI-30-10, 10 mg). During the last 15 s of
the third spin-coating of the perovskite precursor solutions, the DPPS polysilane solution was also spin-coated on the perovskite layer [24]. The prepared cells were then annealed at 180 and 200 °C for 10 min, and at 220 °C for 5 min in ambient air.

Hole transporting layers were spin-coated at 4000 rpm for 30 s. A precursor solution of the hole transporting layer was prepared by mixing chlorobenzene (0.5 mL; Wako Pure Chemical Industries) and spiro-OMeTAD (Sigma Aldrich 36.1 mg) for 24 h. An acetonitrile (Nacalai Tesque, 0.5 mL) solution of lithium bis(trifluoromethylsulfonyl)imide (Tokyo Chemical Industry, 260 mg) was similarly prepared by 24 h stirring. This lithium bis(trifluoromethylsulfonyl)imide solution (8.8 µL) was added to the spiro-OMeTAD solution mixed with 4-tert-butylpyridine (Sigma Aldrich, 14.4 µL) and stirred at 70 °C for 30 min. Lastly, top-electrodes of gold (Au) were formed by a vacuum evaporating system (Sanyu Electron, Tokyo, Japan, SVC-700TMSG). All the fabricated devices were stored at 22 °C and ~30% humidity in ambient air.

The current density voltage characteristics (Keysight, Santa Rosa, CA, USA, B2901A) of the fabricated devices were measured under a solar simulating light source (San-ei Electric, Osaka, Japan, XES-301S) operated at 100 mW cm\(^{-2}\) (air mass 1.5). The exposed area of the photovoltaic devices was 0.080 cm\(^2\). An X-ray diffractometer (Bruker, Billerica, MA, USA, D2 PHASER) was used for microstructural analysis of the perovskite crystals.

3. Results

Conversion efficiencies and other parameters of the present perovskite solar cells are summarized in Table 1, where \(\eta\) is the photoconversion efficiency, \(\eta_{\text{ave}}\) is the average conversion efficiency of the three devices, \(V_{\text{OC}}\) is the open-circuit voltage, \(J_{\text{SC}}\) is the short-circuit current density, \(R_{\text{sh}}\) is the shunt resistance, \(R_{S}\) is the series resistance, and FF is the fill factor. For the as-prepared devices, those annealed at 200 °C exhibited the highest photoconversion efficiencies of 10.99% and 6.20% for MA\(_{0.64}\)FA\(_{0.31}\)K\(_{0.05}\)PbI\(_3\) and MA\(_{0.48}\)FA\(_{0.47}\)K\(_{0.05}\)PbI\(_3\), respectively.

| Devices            | Annealing (°C) | \(J_{\text{SC}}\) (mA cm\(^{-2}\)) | \(V_{\text{OC}}\) (V) | FF  | \(R_{S}\) (Ω cm\(^2\)) | \(R_{\text{sh}}\) (Ω cm\(^2\)) | \(\eta\) (%) | \(\eta_{\text{ave}}\) (%) |
|--------------------|----------------|-----------------------------|----------------------|-----|------------------|------------------|----------|------------------|
| MA\(_{0.64}\)FA\(_{0.31}\)K\(_{0.05}\)PbI\(_3\) | 180            | 13.1                        | 0.383                | 0.333 | 15.53           | 83               | 1.67     | 1.51             |
| MA\(_{0.64}\)FA\(_{0.31}\)K\(_{0.05}\)PbI\(_3\) | 200            | 17.9                        | 0.980                | 0.625 | 7.93            | 177,200         | 10.99    | 7.84             |
| MA\(_{0.64}\)FA\(_{0.31}\)K\(_{0.05}\)PbI\(_3\) | 220            | 13.5                        | 0.864                | 0.573 | 8.18            | 715             | 6.67     | 5.54             |
| MA\(_{0.48}\)FA\(_{0.47}\)K\(_{0.05}\)PbI\(_3\) | 180            | 12.7                        | 0.159                | 0.303 | 7.31            | 26              | 0.613    | 0.381            |
| MA\(_{0.48}\)FA\(_{0.47}\)K\(_{0.05}\)PbI\(_3\) | 200            | 12.6                        | 0.900                | 0.545 | 14.83           | 676            | 6.20     | 4.74             |
| MA\(_{0.48}\)FA\(_{0.47}\)K\(_{0.05}\)PbI\(_3\) | 220            | 10.9                        | 0.871                | 0.604 | 10.67           | 1400           | 5.74     | 4.51             |

After 163 days

| Devices            | Annealing (°C) | \(J_{\text{SC}}\) (mA cm\(^{-2}\)) | \(V_{\text{OC}}\) (V) | FF  | \(R_{S}\) (Ω cm\(^2\)) | \(R_{\text{sh}}\) (Ω cm\(^2\)) | \(\eta\) (%) | \(\eta_{\text{ave}}\) (%) |
|--------------------|----------------|-----------------------------|----------------------|-----|------------------|------------------|----------|-----------------|
| MA\(_{0.64}\)FA\(_{0.31}\)K\(_{0.05}\)PbI\(_3\) | 180            | 20.3                        | 0.970                | 0.700 | 5.12           | 5394           | 13.82    | 12.80           |
| MA\(_{0.64}\)FA\(_{0.31}\)K\(_{0.05}\)PbI\(_3\) | 200            | 19.1                        | 0.966                | 0.595 | 9.00            | 1863           | 10.96    | 9.64            |

XRD patterns of the perovskite solar cells are shown in Figure 2. In all devices, highly (100)-oriented crystals of the perovskite compounds were observed, which were formed by the hot air-blowing method [27]. All devices presented few peaks corresponding to PbI\(_2\), which indicated the effectiveness of the DPPS layer against high-temperature annealing at ~200 °C. Although peaks of lesser intensities, assigned to PbI\(_2\), were observed for the MA\(_{0.64}\)FA\(_{0.31}\)K\(_{0.05}\)PbI\(_3\) devices, especially when annealed at 200 °C, almost no PbI\(_2\) formation was observed for the MA\(_{0.48}\)FA\(_{0.47}\)K\(_{0.05}\)PbI\(_3\) devices, even after annealing at 220 °C. The FA-rich composition contributed to the stability of the cubic perovskite and suppressed PbI\(_2\) formation.
The lattice constants of the perovskites increased as a function of temperature, as shown in Table 2. Additionally, the lattice constant should also increase as FA composition increases because of the larger FA ionic size compared with MA. However, the lattice constant of FA-rich MA$_{0.48}$FA$_{0.47}$K$_{0.05}$PbI$_3$ was smaller than that of MA$_{0.64}$FA$_{0.31}$K$_{0.05}$PbI$_3$, which is suggested to be related with K occupancy at the MA site.

**Table 2.** Measured lattice constants and crystallite sizes of the perovskite compounds.

| Devices             | Annealing (°C) | Lattice Constant (Å) | Crystallite Size (nm) |
|---------------------|---------------|----------------------|-----------------------|
| MA$_{0.64}$FA$_{0.31}$K$_{0.05}$PbI$_3$ | 180           | 6.303(1)             | 77                    |
| MA$_{0.64}$FA$_{0.31}$K$_{0.05}$PbI$_3$ | 200           | 6.302(0)             | 80                    |
| MA$_{0.64}$FA$_{0.31}$K$_{0.05}$PbI$_3$ | 220           | 6.304(1)             | 128                   |
| MA$_{0.48}$FA$_{0.47}$K$_{0.05}$PbI$_3$ | 180           | 6.298(2)             | 86                    |
| MA$_{0.48}$FA$_{0.47}$K$_{0.05}$PbI$_3$ | 200           | 6.299(1)             | 133                   |
| MA$_{0.48}$FA$_{0.47}$K$_{0.05}$PbI$_3$ | 220           | 6.301(0)             | 101                   |
| **After 184 days**  |               |                      |                       |
| MA$_{0.64}$FA$_{0.31}$K$_{0.05}$PbI$_3$ | 180           | 6.294(1)             | 186                   |

**Figure 2.** Measured XRD patterns of the present perovskite solar cells.
Figure 3 shows conversion efficiency changes of the perovskite photovoltaic devices. For the as-prepared devices, those annealed at 200 °C showed the highest conversion efficiencies and were almost identical to the conversion efficiencies after 163 days. Conversely, the conversion efficiency of the MA_{0.48}FA_{0.47}K_{0.05}PbI_3 device, prepared at 180 °C, improved from 0.613% to 8.18% after 109 days, as shown in Figure 3. For the devices annealed at 220 °C, the conversion efficiencies decreased after 50 days.

![Graph showing conversion efficiency changes over time for various perovskite devices.]

Figure 3. Changes of photoconversion efficiencies of the present perovskite photovoltaic devices.

Changes to the J-V characteristics of the MA_{0.64}FA_{0.31}K_{0.05}PbI_3 device, prepared at 180 °C, are shown in Figure 4. For the as-prepared device, the highest conversion efficiency was observed at 1.67%, as shown in Table 1. After 42 days, V_{OC} and J_{SC} were improved. Furthermore, FF also improved after 131 days. After 163 days, the photovoltaic properties of the MA_{0.64}FA_{0.31}K_{0.05}PbI_3 device were further enhanced, and the highest conversion efficiency of 13.82%, a V_{OC} of 0.970 V, a J_{SC} of 20.3 mA cm^{-2}, and a FF of 0.700 were obtained, as shown in Figure 3 and Table 1.

![Graph showing J-V characteristics for various perovskite devices.]

Figure 4. Changes of current density voltage characteristics of the MA_{0.64}FA_{0.31}K_{0.05}PbI_3 device prepared at 180 °C for 10 min.
Microstructural changes of the MA\textsubscript{0.64}FA\textsubscript{0.31}K\textsubscript{0.05}PbI\textsubscript{3} device annealed at 180 °C were investigated by XRD, as shown in Figure 5. Small PbI\textsubscript{2} peaks were observed in both XRD patterns, and further PbI\textsubscript{2} formation was suppressed, even after six months. Full-width at half maximum (FWHM) for the MA\textsubscript{0.64}FA\textsubscript{0.31}K\textsubscript{0.05}PbI\textsubscript{3} device was reduced after six months, which indicated the crystallite size of the perovskite compound increased, as shown in Table 2. The XRD observations indicated the crystal growth of the perovskite compound, which led to a decrease in the grain boundary area and point defects and, hence, improvement in the photovoltaic performance. The lattice constant of the perovskite compound was observed to decrease slightly, as shown in Table 2, which relates to the desorption of a small amount of MA.

![Figure 5. Comparison of the XRD patterns of the MA\textsubscript{0.64}FA\textsubscript{0.31}K\textsubscript{0.05}PbI\textsubscript{3} devices as a function of time, prepared at 180 °C for 10 min.](image)

Conversion efficiencies of polysilane-inserted perovskite solar cells were improved in previous studies [22,24]. The MAPbI\textsubscript{3} device annealed at 190 °C showed an efficiency of 11.57%, which increased to 13.36% after four weeks, and the increases were within 2%. On the other hand, the conversion efficiency of the present solar cell prepared at 180 °C increased from 1.67% to 13.82%, with an increase of efficiency over 12%. To describe this abnormal increase, three mechanisms for the rise in conversion efficiencies of the MA\textsubscript{0.64}FA\textsubscript{0.31}K\textsubscript{0.05}PbI\textsubscript{3} device, prepared at 180 °C, can be considered.

The first is crystallization of the amorphous phase into the perovskite crystal at room temperature. During the spin-coating of DPPS, a mixed composite layer comprising amorphous perovskite and DPPS, having a dense interface, was formed during room temperature aging. In addition, K might compensate MA defects during the aging. Since DPPS also functions as a HTL [20], holes are able to smoothly transport at the perovskite/spiro-OMeTAD interface. Other annealing methods, such as laser-annealing and flash light annealing, have been reported [56,57] and may also be effective for the crystallization of the perovskite compounds.

The second mechanism relates to the formation of a small amount of PbI\textsubscript{2} at the perovskite surface immediately under the DPPS and spiro-OMeTAD layers. A small decrease of the MA\textsubscript{0.64}FA\textsubscript{0.31}K\textsubscript{0.05}PbI\textsubscript{3} lattice constant implies desorption of MA, with PbI\textsubscript{2} suggested to be formed at the surface of the perovskite crystals. PbI\textsubscript{2} is a p-type semiconductor with a bandgap energy of ~2.5 eV and functions as an electron blocking layer [58,59]. Thereafter, FF and conversion efficiency increase.
The third mechanism relates to the interface at the perovskite/spiro-OMeTAD. Since the $V_{OC}$ and $R_{sh}$ had a fairly large increase, the interface would also act as an $n-i-p$ junction instead of the simple back-surface field effect in Si solar cells. The $I-V$ curve as a function of time in Figure 4 demonstrated a typical shape change as the $R_{sh}$ increased. Slow annealing at lower temperatures may provide more uniform and dense perovskite layers.

4. Conclusions

In summary, the influences of DPPS layer insertion between the MA(FA, K)PbI$_3$ perovskite layer and HTL on the microstructures and photovoltaic properties were examined. For the as-prepared devices, those annealed at 200 °C exhibited the highest photoconversion efficiencies, whereas the conversion efficiencies of the devices annealed at 220 °C decreased after 50 days. Conversely, the photovoltaic properties of the MA$_{0.64}$FA$_{0.31}$K$_{0.05}$PbI$_3$ device annealed at 180 °C were improved after 163 days, and the device provided the highest photoconversion efficiency of 13.82%. Microstructures of the perovskite compounds were investigated by XRD, which indicated suppression of PbI$_2$ formation for the DPPS-added device formed at 180 °C, even after six months. Increased crystallite sizes of the MA$_{0.64}$FA$_{0.31}$K$_{0.05}$PbI$_3$ perovskite promoted a decrease of the grain boundary area and point defects, which reduced the current leakage and improved the photovoltaic performance. The present results indicate that polysilane insertion and high-temperature annealing are effective for the improvement of the conversion efficiencies of perovskite photovoltaic devices.

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