Effects of guanidinium addition to CH$_3$NH$_3$PbI$_3$ perovskite solar cells inserted with decaphenylpentasilane

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Abstract: Effects of addition of guanidinium [C(NH$_3$)$_3$; GA] on MAPbI$_3$ perovskite solar cells fabricated at a high temperature of 190 °C in atmospheric air were investigated on the photovoltaic properties and first principles calculations. The addition of guanidinium iodide and the insertion of decaphenylpentasilane between the perovskite and hole transport layer improved the external quantum efficiency and short-circuit current density, and the conversion efficiencies were stable after 1 month. First principles calculations on the density of states and band structures showed reduction of the total energy by the GA addition and the effectiveness of the nitrogen atoms in GA.

Keywords: perovskite; solar cell; methylammonium; guanidinium; polysilane; first principles calculation

1. Introduction

The most common solar cells are currently silicon solar cells. However, the silicon solar cells have a complicated fabrication process and are expensive. Recently developed CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$)-based perovskite compounds have demonstrated numerous advantages, such as tunable band gaps, easy fabrication process, and high conversion efficiencies [1-5]. Higher efficiencies have been accomplished for various perovskite compounds and device structures, and conversion efficiencies above 20% have been achieved [6-14]. However, MAPbI$_3$ perovskite compounds are typically unstable in air because of the migration of CH$_3$NH$_3$ (MA). Therefore, the stability of the corresponding perovskite solar cells should be improved for inclusion in the actual cell module [15]. One method to improve the stability of perovskite solar cells is elemental or molecular adding to the perovskite crystals [16-23].

As guanidinium (C(NH$_3$)$_3$), GA have larger ionic radii (2.78 Å) than MA (2.17 Å), which can be expected to improve the structural stability. Several studies on GA addition have been carried out, and the photovoltaic properties and stability of the MAPbI$_3$ were improved [24-27]. GA addition is expected to extend the carrier lifetime and to reduce the carrier recombination in the perovskite layers [28,29]. In addition to the GA addition, various organic and alkali cations such as formamidinium (CH(NH$_2$)$_2$; FA) [30,31], ethyl ammonium (CH$_3$CH$_2$NH$_3$; EA) [32,33], cesium (Cs) [31,34], rubidium (Rb) [35,36], potassium (K) [21,37], or sodium (Na) [20] were added to stabilize the MAPbI$_3$ perovskite crystals, and the photovoltaic properties were improved by these additions.

Incorporating polymeric materials into the perovskite devices is another approach to improve the stability of perovskite solar cells [38]. For example, coating a thin layer of poly(methyl methacrylate) on top of the perovskite layer forms a cross-linked network structure, which protects the cell from moisture and oxygen [39]. Polysilanes have two
important features. First, polysilanes are p-type semiconductors, which promote hole transfer [40]. Second, polysilanes are more stable at elevated temperatures above 300 °C than ordinary organic materials, which is expected as a protective layer when deposited on perovskite compounds. Therefore, polysilanes, such as decaphenylcyclopentasilane (DPPS), have been applied as HTLs of MAPbI₃ perovskite devices [41,42].

The purpose of the present work is to fabricate and characterize perovskite solar cells in which a small amount of GA was added to MAPbI₃, and annealed at high temperature of 190 °C in ambient air applying the DPPS layer on the perovskite layer. These experimental results were also compared with calculated electronic states and band structures. PbCl₂ and CH₃NH₃PbI₃ were selected to form the perovskite crystals based on the following chemical equation: CH₃NH₃ + PbCl₂ = 2CH₃NH₃Cl + MAPbI₃. The annealing temperature is higher than 140 °C, which may lead the stabilization of the perovskite grains [43]. A small amount of chlorine could improve the diffusion length of excitons and the carrier lifetime, which improved the conversion efficiency [44,45].

Effects of GA adding to MAPbI₃ crystals on the electronic structures were also investigated by first-principles calculation. The effects of GA addition on the microstructures and photovoltaic properties of the MAPbI₃ perovskite solar cells were investigated using current density-voltage (J-V) characteristics, X-ray diffraction (XRD).

2. Experimental procedures

A method for fabricating a perovskite solar cell is shown in Figure 1. Details were described in the previous works [46-50]. F-doped tin-oxide (FTO) substrates were cleaned by using an ultrasonic bath with acetone and methanol, and dried under nitrogen. TiO₂ precursor solutions (0.15 and 0.30 M compact TiO₂) were prepared from titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich, 0.055 and 0.11 mL) with 1-butanol (Nacalai Tesque, 1 mL), and the 0.15 M TiO₂ precursor solution was spin-coated on the FTO substrate at 3000 rpm for 30 s and annealed at 125 °C for 5 min in air to form the compact TiO₂ layer. Mesoporous TiO₂ precursor solution was spin-coated on the compact TiO₂ at 5000 rpm for 30 s and annealed at 550 °C for 30 min in air to form the mesoporous TiO₂ layer.

The perovskite compounds were prepared with N-dimethylformamide (Sigma-Aldrich) of mixing CH₃NH₃I (Tokyo Chemical Industry, 190.8 mg) and PbCl₂ (Sigma-Aldrich, 111.2 mg) at 60 °C for 24 h. This solution was the basic precursor of MAPbI₃, prepared with a mole ratio of 3:1 [43]. MA₀.9Ga₀.1PbI₃ and MA₀.9Ga₀.1PbI₃ precursors were prepared by adding guanidinium iodide (Sigma Aldrich) to control the desired molar ratio. Perovskite precursor solutions were spin-coated on the mesoporous TiO₂ layer three times applying a hot air blowing method during the spin-coatings. The perovskite solutions were spin-coated at 2000 rpm for 60 s. On the third spin-coating, decaphenylcyclopentasilane (DPPS, Osaka Gas Chemicals SI-30-15, 10 mg) solution were dropped on the perovskite layer [42,51,52]. The polysilane solution was prepared by mixing chlorobenzene (Wako Pure Chemical Industry, 0.5 mL) with DPPS. After the spin-coating, the prepared cells were annealed at 190 °C for 10 min in air to form the perovskite layer.

Figure 1. Schematic illustration of the perovskite solar cells.
A hole transport layer was prepared by spin-coating on the perovskite layer. A precursor solution of the hole transport layer was prepared by mixing chlorobenzene and 2,2',7,7'-tetrakis-(N,N-di(p-methoxyphenyl)amine)-9,9'-Spiropyrene (Sigma Aldrich, spiro-OmeTAD) for 12 h. This solution was added that mixing an acetonitrile (Nacalai Tesque, 0.5 mL) with 4-tert-butylpyrididine (Sigma-Aldrich, 188 mg) and lithium bis(trifluoromethylsulfonyl)imide (Tokyo Chemical Industry, 260 mg), stirred at 70 °C for 30 min. Finally, a gold (Au) thin films was evaporated onto the hole transport layer, as top metal electrodes.

The current density voltage characteristics (Keysight B2901A) of the fabricated devices were measured under a solar simulating light source (San-ei Electric XES-301S) operated at 100 mW cm⁻². X-ray diffraction (XRD, Bruker D2 PHASER) was used to investigate the microstructures of the devices.

3. Result and Discussion

Measured photovoltaic parameters are shown in Table 1. The standard cell provided a short-circuit current density ($J_{sc}$) of 19.2 mA cm⁻² and a conversion efficiency ($\eta$) of 11.95%. The addition of 10% GA increased $J_{sc}$ to 21.5 mA cm⁻² from 19.2 mA cm⁻², $\eta$ to 13.88% from 11.95%. The $\eta$ was improved by the GA addition due to the GA and $J_{sc}$ relationship between $J_{sc}$ and $\eta$. The highest $J_{sc}$ and open-circuit voltage ($V_{oc}$) were obtained for the addition of 10% GA, which provided an $\eta_{ave}$ of 13.16%. The average efficiency ($\eta_{ave}$) of three electrodes was measured. After one month, the $\eta$ values for the standard and +GAI cells were stable.

Calculated electronic structures of the MAPbI₃, MA₀.₈₇₅GA₀.₁₂₅PbI₃, and MA₀.₇₅GA₀.₂₅PbI₃ at the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels and the electrostatic potential map are shown in Figure 2, which were calculated by ab-initio methods based on the Hartree–Fock [53-58]. The phases of electron densities in the Pb-6p and I-5p orbitals were inverted, as indicated by the green and red coloration. Since the constructed supercell models are MA-GAPbI₃ and MA-GA₂PbI₃, the chemical compositions are denoted as MA₀.₈₇₅GA₀.₁₂₅PbI₃ and MA₀.₇₅GA₀.₂₅PbI₃, respectively. Although the compositions are not precisely same as those of GA10% and GA 20% crystals, some tendencies on the properties of the crystals could be estimated. The electronic charge of the LUMO showed that the electron would flow straight. The electronic charge of the HOMO was distributed over nitrogen of in the GA, which contributed to the carrier transport and electronic properties. The electrostatic potential was positive (blue) around the methylammonium and guanidinium. Partial density of states (DOS) of the MAPbI₃, MA₀.₈₇₅GA₀.₁₂₅PbI₃, and MA₀.₇₅GA₀.₂₅PbI₃ perovskite crystals are shown in Figure 3. The electrons were increased at -2 eV with the GA addition.

Table 2 shows energy levels of MAPbI₃, MA₀.₈₇₅GA₀.₁₂₅PbI₃ and MA₀.₇₅GA₀.₂₅PbI₃ from the calculation. MAPbI₃ provided a HOMO of -17.78 eV, a LUMO-15.00 eV, Fermi level ($E_F$) of -16.39 eV, band gap ($E_g$) of 1.02 eV. The $E_g$ increased from 1.02 to 0.95 eV by the GA, which may increase the $J_{sc}$ and $\eta$. Gibbs energy ($G$) decreased for structure models by adding GA, which indicates the perovskite crystals are stabilized by the addition of GA.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{sc}$ (mA cm⁻²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$R_s$ (Ω cm⁻²)</th>
<th>$R_{sh}$ (Ω cm⁻²)</th>
<th>$\eta$ (%)</th>
<th>$\eta_{ave}$ (%)</th>
<th>$E_g$ (eV)</th>
<th>$\eta_{ave}$ (After 1 month) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>19.2</td>
<td>0.819</td>
<td>0.760</td>
<td>4.78</td>
<td>635</td>
<td>11.95</td>
<td>11.74</td>
<td>1.546</td>
<td>11.01</td>
</tr>
<tr>
<td>GA 10%</td>
<td>21.5</td>
<td>0.835</td>
<td>0.773</td>
<td>4.66</td>
<td>633</td>
<td>13.88</td>
<td>13.16</td>
<td>1.533</td>
<td>12.36</td>
</tr>
<tr>
<td>GA 20%</td>
<td>21.2</td>
<td>0.793</td>
<td>0.634</td>
<td>7.64</td>
<td>238</td>
<td>10.68</td>
<td>9.84</td>
<td>1.547</td>
<td>9.77</td>
</tr>
</tbody>
</table>
**Figure 2.** LUMO, HOMO, and cutaway view of electrostatic potential for (a) MAPbI$_3$, (b) MA$_{0.875}$GA$_{0.125}$PbI$_3$, and (c) MA$_{0.75}$GA$_{0.25}$PbI$_3$.

**Figure 3.** DOS of MAPbI$_3$, MA$_{0.875}$GA$_{0.125}$PbI$_3$, MA$_{0.75}$GA$_{0.25}$PbI$_3$.

**Table 2.** Energy levels of MAPbI$_3$, MA$_{0.875}$GA$_{0.125}$PbI$_3$ and MA$_{0.75}$GA$_{0.25}$PbI$_3$ calculated by molecular orbital calculation.

<table>
<thead>
<tr>
<th>Structure</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_F$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$G$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI$_3$</td>
<td>-17.78</td>
<td>-15.00</td>
<td>-16.39</td>
<td>1.02</td>
<td>-1470</td>
</tr>
<tr>
<td>MA$<em>{0.875}$GA$</em>{0.125}$PbI$_3$</td>
<td>-17.81</td>
<td>-15.02</td>
<td>-16.42</td>
<td>1.02</td>
<td>-1578</td>
</tr>
<tr>
<td>MA$<em>{0.75}$GA$</em>{0.25}$PbI$_3$</td>
<td>-17.63</td>
<td>-14.94</td>
<td>-16.28</td>
<td>0.93</td>
<td>-1686</td>
</tr>
</tbody>
</table>
Lattice constants of standard, GA10% and GA20% perovskites were measured to be 6.268 Å, 6.276 Å and 6.278 Å, respectively, which indicates an increase by the GA addition. Since the ionic radius of GA⁺ is larger than MA⁺, the increase in the lattice constant would be due to the substitution of GA at the MA-site [1].

The band structures and partial DOS of the MAPbI₃, MAₐₐₜₜGA₀.₁₂₅PbI₃ and MAₐₐₜₜGA₀.₂₅PbI₃ perovskite crystals were calculated by first-principles calculation [59], as shown in Figure 4. Figure 4 shows the 6p orbital of Pb is widely distributed near the conduction band minimum for both crystals. Near the valence band maximum, the 5p orbital of I and the 6s orbital of Pb are distributed. For the MAₐₐₜₜGA₀.₁₂₅PbI₃, the 2p orbital of nitrogen in the GA is distributed at -2 eV, which could promote the improvement of the current density.

Table 3. Band gap and total energies of MAPbI₃, MA₀.₈₇₅GA₀.₁₂₅PbI₃ and MA₀.₇₅GA₀.₂₅PbI₃ by band calculation.

<table>
<thead>
<tr>
<th>Structure model</th>
<th>Band gap (eV)</th>
<th>Total energy (eV cell⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>1.326</td>
<td>-3496</td>
</tr>
<tr>
<td>MA₀.₈₇₅GA₀.₁₂₅PbI₃</td>
<td>1.305</td>
<td>-3629</td>
</tr>
<tr>
<td>MA₀.₇₅GA₀.₂₅PbI₃</td>
<td>1.313</td>
<td>-3629</td>
</tr>
</tbody>
</table>
Electron density distributions of MA$_{0.875}$GA$_{0.125}$PbI$_3$ are shown in Figure 5. The electron density distributions around MA and GA are positively charged. The electron density distribution around GA was slightly lower than that around MA on the Pb-I interfaces, which indicates that carriers around GA would flow and stabilize the perovskite crystals. Table 3 shows the bandgap and total energy of the perovskite crystal lattice obtained from the calculation. The bandgap energies of MAPbI$_3$ and MA$_{0.875}$GA$_{0.125}$PbI$_3$ are calculated to be 1.33 eV and 1.31 eV, respectively. Calculated results on the total energies indicate the GA addition promotes stabilization of the perovskite crystal, which is expected to suppress the desorption of MA or GA. The GA addition also causes a reduction in the bandgap and increases the number of excited electrons.

4. Conclusions

EQE and $j_{sc}$ were improved by the GA addition to the MAPbI$_3$. The $\eta$ of 12% was maintained for the GA10% added device even after 1 month. The synergistic effect of the addition of GA and insertion of polysilane for the high temperature fabrication of solar cells is effective for stabilization of perovskite solar cells. From the results of first-principles calculations, the carrier transport was changed by the GA addition.


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