The Temperature Effect on the Working Characteristics of Solar Cells Based on Organometal Halide Perovskite Crystals

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Abstract. Organometal halide perovskites have been much studied as an active material in a new generation of solar cell with high power conversion efficiency. The chemical reactions involved in their crystallization process are simple but the crystallization process and the formed crystal are very sensitive to temperature and humidity. In general, if the electronic structure of this active material is easily affected by temperature, the working performance of its solar cell will be also easily affected by temperature. In this work, we investigated the temperature effect on the working performance, namely the $J$-$V$ characteristics, of CH$_3$NH$_3$PbI$_3$ perovskite based solar cell. The measurement result show that the $J$-$V$ characteristic significantly changed with temperature. The $J$-$V$ curve shows a diode characteristic at room temperature but it changes to an Ohmic characteristic at high temperature. This characteristics change may be due to the degradation of the perovskite crystals, which may be caused by separation and recrystallization PbI$_2$ inside the perovskite layer.

1. Introduction
Two research groups led by Snaith and Grätzel have independently reported the use of organometal halide perovskite as active material for a new generation of highly efficient solar cells. Since then the study of this material as an active layer for solar cells has attracted much attention and rapidly developed. [1-4] This perovskite crystal contains organic group, which is different from conventional inorganic perovskite crystals that have been known for long time. In general, these crystals have a similar structure as calcium titanium oxide (CaTiO$_3$). The general formula to represent perovskite structure is AMX$_3$, where 'A' and 'M' are two cations with different size and X is an anion. The ideal cubic-symmetry structure has the M cation in 6-fold coordination that is surrounded by an octahedron of anions (MX$_6$), while the A cation in 12-fold cuboctahedral coordination, as illustrated in Figure 1a and 1b. The organometal halide perovskite, such as methylammonium lead tri-iodide (MAPbI$_3$), has the same the AMX$_3$ formula, where CH$_3$NH$_3^+$ (MA$^+$) is as the A cation, Pb$^{2+}$ is as the M cation, and I is as the X anion.
Conventional inorganic perovskite crystals have been much studied in relation to their magnetic and electronic properties including ferroelectricity and the superconductivity properties. Most of inorganic perovskite crystals are stable. In contrast to those perovskite crystal, organometal halide perovskite crystals exhibits photovoltaic and other photoresponsive properties. Organometal halide perovskite, such as CH$_3$NH$_3$PbI$_3$, can be prepared by a simple chemical reaction, namely:

$$\text{PbI}_3\text{ (s)} + \text{CH}_3\text{NH}_3\text{I (aq)} \leftrightarrow \text{CH}_3\text{NH}_3\text{PbI}_3\text{ (s)} \quad (1)$$

However, the chemical stability during the crystal formation and fabrication processes should be always taken into consideration. [5-6] Oxygen and moisture in the atmosphere have crucial effects leading to the degradation of perovskite crystal, which may occur through the following reactions:

$$\text{CH}_3\text{NH}_3\text{PbI}_3\text{(s)} \leftrightarrow \text{PbI}_2\text{(s)} + \text{CH}_3\text{NH}_3\text{I (aq)} \quad (2)$$

$$\text{CH}_3\text{NH}_3\text{I (aq)} \leftrightarrow \text{CH}_3\text{NH}_3\text{H}_2\text{(aq)} + \text{HI (aq)} \quad (3)$$

$$4\text{HI (aq)} + \text{O}_2\text{(g)} \leftrightarrow 2\text{I}_2\text{(s)} + 2\text{H}_2\text{O (l)} \quad (4)$$

$$2\text{HI (aq)} \leftrightarrow \text{H}_2\text{I}_2\text{(g)} + \text{I}_2\text{(s)} \quad (5)$$

It is also evident that the formed crystal structure significantly affected by temperature. The perovskite crystals shows three phases, namely $\alpha$, $\beta$, and $\gamma$ phases, depending on the temperature. [7-9] This paper presents a report concerning the temperature effect on the $J$-$V$ characteristics of this perovskite solar cell.

2. Experiments

The structure of the solar cell investigated here is a multilayer structure of FTO/c-TiO$_2$/mp-TiO$_2$/Perovskite/spiro OMeTAD/Au, as illustrated in Figure 3. Compact TiO$_2$ (c-TiO$_2$) layer was used as the blocking layer and the mesoporous TiO$_2$ (mp-TiO$_2$) was used as the scaffold mesopori layer. This layer was deposited on the top of FTO substrate by using a spincoater at 5000 rpm for 30 s with acceleration 2500 rpm/s. The layer was sintered up to 550°C for the c-TiO$_2$ and 475°C for the mp-TiO$_2$ layer.

In order to prepare the perovskite crystal in TiO$_2$ mesoporous layer, a precursor solution of perovskite was deposited by one step precursor deposition method at 3000 rpm for 30 s. The precursor solution have 1:1 mol ratio of the PbI$_2$ and MAI in the DMF. This solution was previously heated at 120°C for 20 minutes to promote complete dissolution and is preserved at 70°C before spin coating process.

The spiro-OMeTAD as the hole transport material (HTM) was deposited on the top of perovskite layer by using a spincoater at 5000 rpm for 30 s. Spiro-OMeTAD solution was prepared from a chlorobenzene solution containing 72.3 mg/mL spiro-OMeTAD, 17.5 $\mu$L/mL of LiTFSI stock solution (stock: 520 mg/mL LiTFSI in acetonitrile), and 263 $\mu$L/mL of FK 102 Co(III) TFSI stock

![Figure 1. (a) Crystal structure of cubic perovskite with general formula of AMX$_3$; (b) Twelve-fold coordination of the A-site cation. [2]](image)

![Figure 2. The crystal structure of organometal halide perovskite with MA$^+$ as the A cation.](image)
solution (stock: 300 mg/mL FK102 in acetonitrile). Finally, Au layer was deposited by using physical vapour deposition as the electrode.

Figure 3. The structure of the perovskite solar cell investigated here.

Figure 4. The measured J–V characteristic of a perovskite solar cell sample fabricated in this work under light illumination (1 sun).

3. Results and Discussion

Figure 4 shows typical characteristic of J-V curve measured from perovskite solar cells fabricated in this work. This sample shows the efficiency, short circuit photocurrent ($J_{sc}$), open voltage bias ($V_{oc}$), and Filling Factor (FF) of about 4.3%, 11.5 mA/cm$^2$, 0.63V and 0.58, respectively. In order to study the effect of temperature on the solar cells, the J-V characteristics of the cells were measured under dark condition. Figure 5 (a) and (b) clearly shows that the J-V characteristic is significantly affected by temperature. At room temperature, the J-V curve exhibits a diode characteristic. However, it much deviates from a diode characteristic at high temperature.

Figure 5. The measured J–V characteristic of this perovskite solar cell at various temperatures presented in (a) in normal scale and (b) in logarithmic scale for both x-axis and y-axis.
For understanding the change on these $J$-$V$ characteristics, the curves were fitted by the Murgatroyd equation. [10] However, the fitting for temperature larger room temperature were failed if we did not add an additional parameter that is related to an internal resistance $r$. The fitting equation then becomes

$$J_{SCLC} = \frac{9}{8} \mu \frac{(V - V_{bi})^2}{d^3} \exp \left( \frac{0.98 \beta \sqrt{V - V_{bi}}}{\sqrt{d}} \right) + \frac{V}{r}$$

where $\mu$ is the mobility, $\varepsilon$ is the permittivity, $\beta$ is the Poole–Frenkel parameter for taking into account the electric field-activation factor and the degree of disorder, $V_{bi}$ is built-in potential, and $d$ is the thickness of perovskite layer. The second term in eq. (6) is introduced to represent Ohmic medium governed by PbI$_2$ crystals inside the perovskite layer, where the amount of this PbI$_2$ crystals may increase when the cell degrades. The fitting results are shown in Figure 6, while the fitting parameters are tabulated in Table 1.

![Figure 6](image-url)

**Figure 6.** Fitting results of the $J$-$V$ curves using eq. (6) for measurements at (a) 30°C, (b) 60°C, (c) 70°C and (d) 90°C.

In a solar cell, Schottky barrier (SB) may be formed at the interface between two semiconductors or between semiconductor and metal. The Schottky barrier causes the formation of built-in potential ($V_{bi}$) because the Fermi energy alignment causes the energy bending of valence band and conduction band. The observation of a diode characteristic measured at room temperature here may suggest the formation of built-in potential. As indicated in Table 1, the built-in potential values are zero for
measurements above the room temperature. On the other hand, the internal resistance associated with $r$ parameter decreases significantly with the increase of temperature. This may indicates the change of perovskite layer from semiconductor to Ohmic materials. Such situation may occur due to the degradation of perovskite layer, which possibly by separation of the inorganic and organic entities producing separate phases of PbI$_2$ and MAI again.

4. Conclusion

The measurement results show that the $J$-$V$ characteristic of this perovskite solar cell is significantly affected by temperature. The $J$-$V$ curve measured at room temperature has a diode characteristic. However, the fitting results indicate that the solar cell loses the diode characteristic and turns into Ohmic characteristic at higher temperature. This may be due to the degradation of the perovskite crystal at temperature, which may be caused by separation and recrystallization PbI$_2$. Special attention to overcome this problem is required for improving the stability of this solar cell performance.

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