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Investigation of the Stability of absorption Layer in Perovskite Solar Cell

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ABSTRACT
Organic-inorganic hybrid perovskite was first published as a light absorbing material in solar cells since 2009. After years of research, the efficiency of perovskite solar cells has increased from about 3% to more than 20%. As a kind of clean and safe renewable energy, perovskite-based solar cell has the advantages of simple preparation process, low cost and promising commercial value. However, the stability of perovskite film is poor, which hinders its further application. In this study, two-step method was utilized to prepare the absorption layer of perovskite solar cells and the stability of the absorption layer was investigated at different humidity and temperature conditions. The results showed that perovskite structure was easy to decompose under high temperature or humidity environment, which was the origin of instability of perovskite film.

KEYWORDS
Stability; Microstructure

1 Introduction

Solar energy is available, clean and environmental-friendly and is one of the abundant renewable energy resources. Perovskite solar cell (PSC) is a new type of solar cell derived from Dye sensitized solar cell (DSSC). It was first proposed by Kojima(1), a scientist from Japan and its structure followed DSSC. He replaced the commonly used organic dyes with CH_3NH_3PbI or $CH_3NH_3PbBr_3$ and the PCE (photovoltaic conversion efficiency) of the solar cell is more than 3%. Since $CH_3NH_3PbX_3$ has perovskite crystal structure, this type of solar cells is referred to as perovskite solar cell. Compared with organic photovoltaic (OPV), DSSC, and amorphous silicon (a-Si) solar cells, the efficiency of perovskite solar cells has been improving rapidly. In 2009, the photovoltaic conversion efficiency of perovskite solar cells was just 3.8%. However, in early 2014, KRICT (Korea Research Institute of Chemical Technology) increased the efficiency to 17.9%. And in May 2014, the Yang team at the University of California, Los Angeles (UCLA) had already increased the efficiency to 19.3%. Additionally, in November 2014, the team had achieved a further increase in the efficiency, bringing it up to 20.1%. Nowadays, the PCE of perovskite solar cells has increased to 22.1%(2) and is expected to reach to the PCE of monocrystalline silicon solar cells (25.6%).

Lead halide perovskite, which is an organic-inorganic hybrid material with the chemical formula ABX_3 (where A:$CH_3NH_3^+$; B: Pb^{2+}; X: I^-, Br^- or Cl^-), possess a typical perovskite ($CaTiO_3$) crystal structure. PbX_6 forms octahedrons that constitute a three-dimensional structural framework, with $CH_3NH_3^+$ embedded within it. Due to the photoluminescence and electroluminescence properties of ABX_3, it was initially studied as an active layer for light-emitting diodes and field-effect transistors. In recent years, researchers have found that $CH_3NH_3PbX_3$ possesses almost all the conditions for a perfect light-absorbing material: a high absorption coefficient, excellent carrier transport properties, a suitable direct bandgap, and extremely high defect tolerance. As a direct bandgap semiconductor, $CH_3NH_3PbX_3$ exhibits strong light absorption for photons with energy greater than the bandgap width. Its absorption coefficient is even comparable to that of amorphous silicon, and a perovskite material with a thickness of around 300 nm can absorb almost all visible light. As a result, this type of materials has good application prospects(3). However, according to research, in an environment with high temperature or high humidity, crystal lattice of perovskite structure will be easily destroyed so that the material will decompose. Therefore, this article will discuss the stability of perovskite from the perspectives of material structure and morphology.

2 Experimental steps

Place a cleaned glass slide on a spin coater, use a pipette to take 30 microliters of lead iodide DMF solution and drop it evenly on the glass slide. Set the rotation speed to 3000 rpm and the spin coating time to 50 seconds. After the spin coating, dry the film at 70℃ for 30 minutes. Subsequently, immerse the lead iodide film in a solution of methylammonium iodide in isopropanol for 20 seconds, then take it out and dry it at 70℃.

Perform heat treatment on the perovskite solar cell light-absorbing layer prepared by the two-step method at temperature of 150℃, 200℃, 250℃, and 300℃ to study its temperature stability. Place the film in a constant temperature and humidity chamber with temperature controlled at 22℃ and humidity adjusted to 50%, 70% , and 90% to study its humidity stability. The morphology and structure of the film are characterized by field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD).

3 Experimental result and analysis

3.1 Temperature stability of light-absorbing layer

The color of prepared light-absorbing layer is red-brown. Under the condition with temperature at 150℃, after 7 minutes, the red-brown color begins to fade, gradually turning to yellow from the edges to the center. It becomes transparent at 12 minutes and completely turns yellow after hail an hour. Under the condition with temperature at 200℃, the color begins to change after 30 seconds, the red-brown color fading and yellow appearing at the edges. It completely turns to yellow after 3 minutes and then the color gradually turns to orange. After the color stabilizes, remove it and cool it to room temperature (22℃) , where the color turns from orange to yellow. Under the condition with temperature at 250℃, the color begins to change in 15 seconds and completely turns to yellow after 30 seconds. Under the condition with temperature at 300℃, it turns to yellow in 10 seconds and then instantly turns to orange. When placing it at room temperature, it turns to yellow.

The scanning electron microscopy images of the untreated two-step method-prepared light-absorbing layer are shown in Figure 1. a and 1. b. From the image, it can be observed that the perovskite film prepared by the two-step method has a dense block-like structure, with the size of the block-like grains approximately 250 nm, which is consistent with literature reports(4). The scanning electron microscopy images after heat treatment at 150℃, 200℃, 250℃, and 300℃ are depicted in Figure 1. After treatment at 150℃, the film turns from a blocky crystalline structure to a lamellar structure, with the size of nanosheet about 300nm. As the temperature increases, the size of nanosheet gradually becomes bigger. When the temperature increases to 300℃, the surface of the nanosheet becomes smooth, and the size increases to around 1-2 micrometers. Combined with the XRD results (Figure 2) , we find that the perovskite film undergoes decomposition after temperature treatment and the composition of the film turns to yellow PbI_2(5). In the figure, the XRD diffraction peaks at room temperature appear at 2θ=14.82°, 28.40°, 31.86°, 40.49°, 43.19°, which are obvious diffraction corresponding to the perovskite(6). Among them, the peak at 2θ=14.82° corresponds to crystal plane (110) of the perovskite crystal, indicating that the perovskite film prepared by us possesses good crystallinity. The XRD diffraction peaks treated at different temperatures appear together at 2θ=12.71°, 34.30°, 52.4°, which are the characteristic diffraction peaks of the (001), (002) and (004) crystal planes of PbI_2, indicating perovskite treated at different temperature commonly undergoes decomposition. According to the experimental phenomenon, film treated at 150℃ completely decomposes after half an hour while film treated at 300℃ decomposes into lead iodide after 15 seconds, which indicates the perovskite materials have poor temperature resistance.

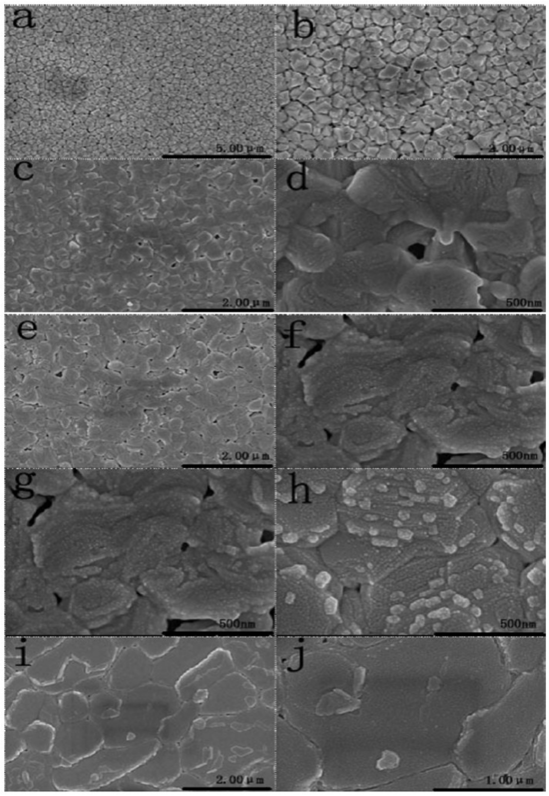

Figure 1 FESEM images of perovskite films at different temperature

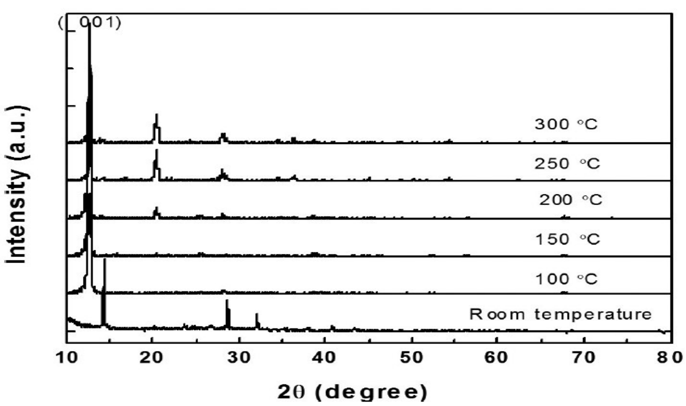

Figure 2 XRD images of perovskite films at different temperature

3.2 Humidity stability of light-absorbing layer

Under the condition of 50% humidity, the color of the sample doesn't change obviously in four hours. Starting from six hours, the edges begin to turns to yellow, and the film completely turns to yellow after 12 hours. Under the condition of 70% humidity, the edges begin to turns to yellow in 3 hours and completely turn to yellow after 12 hours. While under the condition of 90% humidity, the edges begin to become yellow in 5 minutes and completely turns to yellow after 20 minutes.

The scanning electron microscopy figures of light-absorbing layer treated at 50% humidity are shown in Figure 3.a and 3.b. When the film treated at 50% humidity turns to yellow, as can be seen in the image, film begins to turns from a block-like structure to a lamellar structure. From XRD image (Figure 4), it can be observed that film untreated is perovskite possessing good crystallinity, and for film treated at different humidity, the characteristic peak at 2θ =14.82° disappears while the characteristic peak appears at 2θ=12.71°, which indicating after humidity treatment perovskite film commonly turns to PbI2 film. It indicates that perovskite materials have poor humidity resistance.

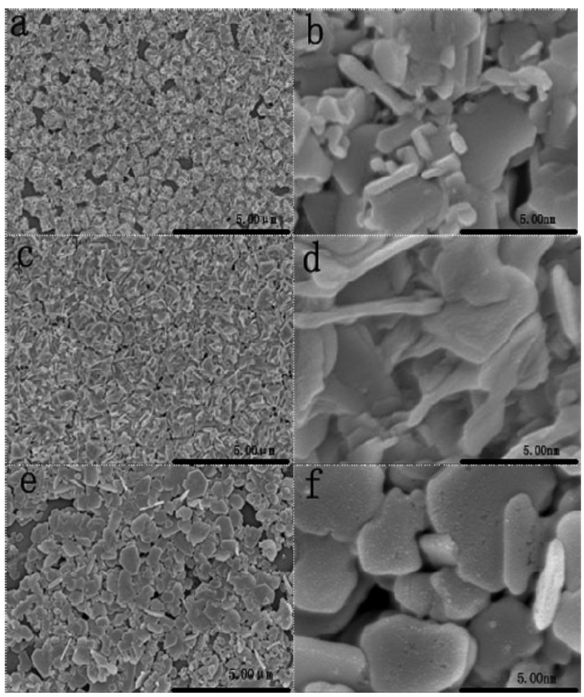

Figure 3 FESEM images of perovskite films at different humidity

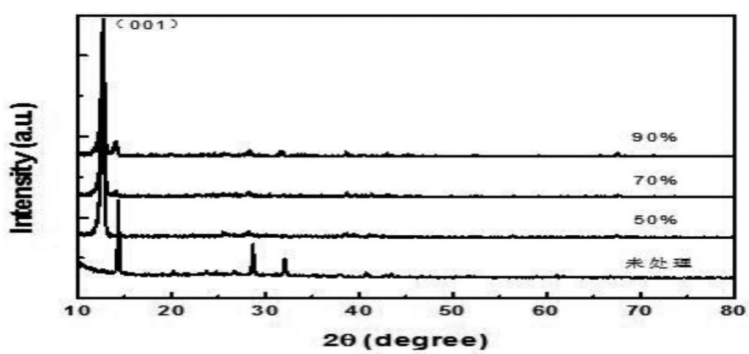

Figure 4 XRD images of perovskite films at different humidity

4 Conclusion

We prepare perovskite films by the two-step method and study influence that temperature and humidity have on morphology and structure of film by scanning electron microscope and XRD. The result indicates that perovskite film has poor temperature and humidity resistance. Film treated at 150℃ or higher temperature is about to decompose into PbI_2 and its morphology turns from block-like to lamellar. As temperature increases, the diameter of lamellar structure gradually increases from about 300nm to 1-2 micrometers. Film begins to decompose placing in the air with humidity of 50% for 6 hours while the discoloration of film placing in the air with a humidity of 90% is shortened to 5 minutes. At the same time, film turns from a blocky structure to a lamellar structure of PbI_2. The temperature and humidity resistance remain to be further improved, which is one of the significant challenges in the commercialization process of perovskite solar cells.

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