Fabrication and characterization of Cs_2SnI_6 perovskite films using SnI_2 and I_2 powders as reactants

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Abstract

In the recent years, cesium tin iodide (Cs_2SnI_6) double perovskite has emerged as a research hotspot in photovoltaics due to its exceptional stability and outstanding optoelectronic properties. In this work, we have utilized a reactant combination of SnI_2 and I_2 to prepare uniform Cs_2SnI_6 films via modified two-step process. The impact of the reaction conditions on the structural, morphological and optical properties is explored. It is found that optimizing the reaction conditions improves the phase stability and morphology of the films. The iodine-rich fabrication of the films ensued in enhanced PL and optical characteristics of the Cs_2SnI_6 with an optimal bandgap in the range of 1.21-1.34 eV. Additionally, we constructed all-inorganic photovoltaic devices $\text{FTO}/\text{TiO}_2/\text{Cs}_2\text{SnI}_6/\text{Carbon}$ utilizing optimized Cs_2SnI_6 films.

1. Introduction

To circumvent Pb toxicity, tin-based halide compounds are being extensively investigated owing to its excellent optoelectronic characteristics and low toxicity [1–2]. Amongst the possible substitutes, the vacancy-ordered double perovskite (A_2BX_6), a class of halide perovskite compounds, has garnered interest as a Pb-free contender for photovoltaic applications [3–5]. Among them, a seldom investigated perovskite variant material Cs_2SnI_6 , has lately attracted considerable attention in the field of photovoltaics due to its low toxicity, air stability, and excellent optoelectronic properties [6–9]. Cs_2SnI_6 is an excellent alternative to Pb-Perovskite solar cells (PSCs) due to the stable +4 oxidation state of the Sn atom. Numerous theoretical and experimental studies have been published to shed light on the structural, optical, electrical, and intrinsic defect features of A_2BX_6 derivatives [10–14]. Qiu et al. [5] explored the Cs_2SnI_6 perovskite as a viable light-absorbing material for the first time and obtained promising power conversion efficiency (PCE) of 0.96 %. Numerous theoretical and experimental studies have been published to shed light on the structural, optical, electrical, and intrinsic defect features of A_2BX_6 derivatives [10–14]. Until now, no major progress toward efficient Cs_2SnI_6 devices has been accomplished, and the PCE remains low (1%). The main reason for the low performance of is attributed to the high conductivity of Cs_2SnI_6 produced by iodine vacancies and CsI impurities. Numerous studies have documented the use of a variety of deposition procedures and processing routes to improve the parameters of Cs_2SnI_6 perovskite [10–18]. Vapor processing of two precursors is a feasible way to fabricate high-quality Cs_2SnI_6 perovskite films. In general, CsI and SnI_4 are capable of forming stoichiometric Cs_2SnI_6 films devoid of impurity phases. However, SnI_4 is not recommended for thermal evaporation due to its susceptibility to thermal deterioration and inability to form a uniform layer [10]. Therefore, SnI_2 was chosen as a precursor material for this work. Furthermore, the CsI impurity and iodine vacancy defects can be inhibited with the introduction of I_2 . In this work, we have introduced a new combination of reactants to fabricate uniform Cs_2SnI_6 films. The introduction of I_2 plays critical role for achieving the correct stoichiometry and for providing extra iodine to minimize defect density in the

Cs₂SnI₆ perovskite. Furthermore, the effect of reaction conditions on the films optoelectronic properties is thoroughly investigated.

2. Experiment Details

The first step involved the preparation of CsI films with fixed thickness using electron beam evaporation method. Using a combination of SnI₂ and I₂ we thermally evaporated the powders onto the resultant CsI films to prepare crystal-black Cs₂SnI₆ films. The reaction was carried out using stoichiometric amounts of the powder in a closed reactor inside an oven. The reaction temperature for the first series of the samples was kept fixed at 220°C, while the reaction time was varied to 80 mins, 60 mins and 40 mins. For the second series, the Reaction time is fixed for 1 hour and the reaction temperature is varied as 220°C, 190°C, and, 160°C. The goal of this proposed strategy was to improve the utilization of the powders and inhibit the decomposition of Cs₂SnI₆ films.

2.1 Characterization

The structural properties of the films were determined using a CuK α -irradiated x-ray diffractometer (XRD, X'Pert PRO). Scanning electron microscopy (SEM, JEOL, JSM-6700 F) was used to examine the films' morphology. A UV–vis–NIR spectrophotometer (HITACHI UH4150) was used to determine the optical properties in the 400–1100 nm region. A Laser Raman Spectrometer was used to perform PL and Raman measurements (LabRAM HR Evo). The observations were conducted at a 633 nm excitation wavelength. The solar cells' current-voltage (I-V) curves were measured using a Keithley 2400 source meter and a constant sun illumination (AM 1.5 G, 100 mW/cm²).

3. Results And Discussion

Figure 1(a-c) shows the XRD reflections of the grown films as a function of reaction time (at 220°C). Crystal reflection indices and secondary phases have been allocated to the corresponding films. All of the films' XRD data designate that the crystal structure is in good conformity with that of the Cs₂SnI₆ structure (JCPDS No. 51-0466, space group Fm3m). The primary intensity peaks corresponds to the atomic planes of (222), (004), and (044), respectively. The Cs₂SnI₆ film grown for 60 minutes also contains a tiny amount of CsI and SnI₂ with secondary phases at 24.5 and 27.5°. At higher reaction temperatures, the CsI impurity peak is often generated by the decomposition of Cs₂SnI₆ perovskite. However, the amount of this impurity is quite small, implying that the presented approach is capable of producing highly crystalline Cs₂SnI₆ films.

The lattice strain factor (ϵ) and average crystallite size of the fabricated films were calculated using the Williamson-hall plot method, which is given as follows

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta \quad (1)$$

Here, the ϵ is calculated by the slope of fitted lines while the average crystallite size is calculated from the y-intercept of the plot, as depicted in Fig. 1(d-f). The average crystallite size of the film decreased substantially with the increase in the reaction time. Furthermore, the calculated values of the crystallite size and lattice strain are finely consistent with the theoretical model and literature reports on Cs_2SnX_6 [19].

The optical characteristics of the Cs_2SnI_6 films were determined using the UV-Vis-NIR absorption spectrum. As shown in the Fig. 2(a), the absorption edge of Cs_2SnI_6 shifted to higher wavelengths as the reaction time decreased. The optical bandgap (E_g) of films was determined using the Tauc plots in Fig. 2(b), where $(h\nu)$ is plotted along the X-axis and $(\alpha h\nu)^2$ is plotted along the Y-axis. To determine the bandgap value, the straight-line component of the plot was extended to span the X-axis. The samples had E_g values of 1.34, 1.27, and 1.22 eV for Cs_2SnI_6 films made at 80, 60, and 40 minutes, respectively. These values are consistent with the range of values previously reported for Cs_2SnI_6 perovskite materials (1.2-1.7 eV) [10-11]. The Photoluminescence (PL) spectra at room temperature stimulated by a 633 nm laser are depicted in Fig. 2(c). A strong PL peak extending from 800 to 900nm was seen, with the peak centered around 860-880 nm, indicating that the films' bandgaps match the values derived from the Tauc plot. With decreasing reaction time, we found a minor change in peak position toward the higher wavelength, which was also detected in absorption spectra.

The morphological examination of Cs_2SnI_6 films fabricated under various reaction time is shown in Fig. 3(a-c). The primary objective of this investigation was to determine the impact of reaction time on the growth and morphology of the crystallites. The morphology of the fabricated films is dominated by homogeneous and truncated octahedrons and tetrahedrons with uniform surface coverage and grain sizes ranging from a few micrometers to several micrometers. The films are highly dense, uniform, and free of pinholes, which is crucial for photovoltaic applications. At 80 minutes, the film reveals microscopic grain sizes and a significantly rougher morphology. By reducing the reaction time to 60 and 40 minutes, the grain size increased dramatically, implying that the films have a lower overall surface to volume ratio, and hence should exhibit increased resistance to the ambient atmosphere and stability. Additionally, small white pores can be detected in the corresponding SEM images, which may be generated by residual SnI_2 vapor bound to the outermost surface of the Cs_2SnI_6 films in the closed reactor. Additional investigation of the grain size indicated that as the reaction time changes, the grain size fluctuate, as illustrated in Fig. 3(d-e). As seen in Fig. 3(f), the EDS spectra reveal the existence of Cs, Sn, and I elements with no significant impurity peaks.

We further investigated the role of reaction temperature on the properties of Cs_2SnI_6 films. To investigate the films' vibrational properties, Raman spectra were recorded using a 633 nm excitation wavelength, as illustrated in Fig. 4. The Raman spectrum of Cs_2SnI_6 films synthesized at various reaction temperatures

provides more evidence for the perovskite modified structure. Six distinct symmetric stretching vibration modes ($m_1 - m_6$) exist for $[\text{SnI}_6]^{2-}$ octahedral in Cs_2SnI_6 , among which m_1 , m_2 , and m_5 are Raman-active. Three prominent peaks in the spectra at 126 cm^{-1} , 92 cm^{-1} , and 78 cm^{-1} correspond to Cs_2SnI_6 Raman-active modes. There are some secondary phase peaks seen in the 160°C samples, indicating that the low reaction temperature may not result in the formation of the pure phase Cs_2SnI_6 . At 249 cm^{-1} , an additional higher order mode was detected, which is ascribed to the strong resonance circumstances.

The absorbance spectrum of Cs_2SnI_6 thin film was examined in the wavelength range of 500-1000 nm in order to regulate its optical characteristics (Fig. 5a). As shown in (Fig. 5b), the absorption edge maintained a blue shift as the reaction temperature decreased. From Fig. 5b, the absorption onsets revealed that the films had E_g values of 1.27, 1.28, and 1.25 eV for Cs_2SnI_6 films formed at 220°C , 190°C , and 160°C minutes, respectively. The optical band gap was also confirmed using the room temperature PL spectrum, as depicted in Fig. 5c. A prominent PL peak was observed spanning from 800 to 900 nm, with the peak positioned around 860-880 nm, showing that the films' bandgaps complement the values estimated from the Tauc plot. The PL and absorption analyses show that the fabricated Cs_2SnI_6 has a direct band gap, which is in agreement with findings in the literature [10].

To characterize the photovoltaic device, we constructed it using the Cs_2SnI_6 film (60 minutes at 220°C) in the planar device design represented in Fig. 6a. Fig. 6(b) shows the energy band diagram and a characteristic cross-sectional view of the perovskite layers. Unfortunately, the device exhibited low PCE and a low current voltage (V_{oc}) (Fig. 6c). The basic explanation for the low PCE is believed to be a combination of factors. To begin, Cs_2SnI_6 phase stability and crystallinity should be enhanced further. Second, by optimizing the electron and hole transporting layers, it is possible to increase the efficiency of power conversion by lowering the series resistance and increasing the shunt resistance. Additionally, the high electrical resistance of Cs_2SnI_6 might result in low FF and current density values. Our findings, we hope, will open up new avenues for the fabrication of efficient and stable Cs_2SnI_6 devices.

4. Conclusion

In summary, we used a reactant mixture of SnI_2 and I_2 to fabricate uniform Cs_2SnI_6 films using a modified two-step technique. With optimization of the reaction conditions, the obtained films demonstrated increased crystallinity and homogeneous morphology. UV-vis absorption and photoluminescence investigations verify the direct nature of Cs_2SnI_6 , which has a bandgap ranging from 1.21 to 1.34 eV. Additionally, we showed its use as an absorbent layer in a planar solar cell configurations consisting of $\text{FTO}/\text{TiO}_2/\text{Cs}_2\text{SnI}_6/\text{C}$. Efforts are now being made to increase the device's efficiency.

Declarations

Acknowledgments

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Declaration of interests

☐ The authors state that they have no known competing financial or personal affiliations that could have influenced their work.

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Figures

Figure 1

(a) XRD patterns of Cs₂SnI₆ films prepared at (a) 80 mins (b) 60 mins (c) 40 mins, and strain factor of the films at (d) 40 mins and (e) 60 mins, (f) Average crystallite size of the films deposited at different

reaction time.

Figure 2

(a) Optical absorption spectrum (b) Tauc plots and (c) PL spectrum of the films deposited at different reaction time.

Figure 3

(a) SEM micrographs of the Cs_2SnI_6 films deposited at (a) 40 mins (b) 60 mins (c) 80 mins, Grain size estimation of the films at (d) 40 mins (e) 60 mins, (f) EDS spectrum of the 60 mins reacted film

Figure 4

Raman spectrum of the films deposited at different reaction time.

Figure 5

(a) Optical absorption spectrum (b) Tauc plots and (c) PL spectra of the films deposited at different reaction temperatures.

Figure 6

(a) Structure of planar PSC device. (b) Energy band structure of the device. (c) The J-V curve.