# Role of precursor solution in controlling the opto-electronic properties of spray pyrolysed $Cu_2ZnSnS_4$ thin films

V.G. Rajeshmon [a], C. Sudha Kartha [a], K.P. Vijayakumar [a,*], C. Sanjeeviraja [b], T. Abe [c], Y. Kashiwaba [c]

[a] Department of Physics, Cochin University of Science and Technology, Cochin 682 022, India
[b] School of Physics, Alagappa University, Karaikudi 630 003, India
[c] Department of Electrical and Electronic Engineering, Iwate University, Morioka 020-8551, Japan

## Abstract

Thin films of $Cu_2ZnSnS_4$, a potential candidate for application as absorber layer in thin film solar cells, were successfully deposited on soda lime glass substrates using spray pyrolysis and the effect of variation of precursor on the structural and opto-electronic properties was investigated. We used stannous as well as stannic chloride as precursors of tin in the spray solution. All the films exhibited kesterite structure with preferential orientation along the (1 1 2) direction. But crystallinity and grain size were better for stannic chloride based films. Also they possessed a direct band gap of 1.5 eV and the absorption coefficient was $>10^4 \, \text{cm}^{-1}$. Carrier concentration and mobility could be enhanced and the resistivity reduced by two orders by using stannic chloride in spray solution. Junction trials were performed with CZTS films prepared using stannic chloride precursor as the absorber layer and indium sulfide as the buffer layer. XPS depth profiling of the junction was done. Formation of CZTS could be confirmed and also information about the junction interface could be obtained from the XPS results. We obtained an open-circuit voltage of 380 mV and short-circuit current density of 2.4 mA/cm$^2$.
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Keywords: Thin films; Spray pyrolysis; Precursor solutions; Solar cell

## 1. Introduction

$Cu_2ZnSnS_4$ (CZTS) is one of the most promising materials for absorber layer in thin film solar cells because of the suitable optical band gap of about 1.5 eV, a high absorption coefficient greater than $10^4 \, \text{cm}^{-1}$ and easy availability as well as eco-friendly nature of the constituent materials. It is obtained by replacing half of the indium atoms in chalcopyrite $CuInS_2$ with zinc and the other half with tin. CZTS thin films possess superior optoelectronic characteristics and hence have been investigated as a highly potential candidate for absorber layer in thin film solar cells. A thorough understanding of the material properties is very much essential for successful utilization of this compound semiconductor in solar cells.

Thin films of CZTS can be prepared using several techniques such as co-evaporation (Tanaka et al., 2006), hybrid sputtering (Tanaka et al., 2005), RF magnetron sputtering (Seol et al., 2003), pulsed laser deposition (Sekiguchi et al., 2006; Moriya et al., 2007; Moriya et al., 2008), sulfurizing sol–gel deposited precursors (Tanaka et al., 2007; Miyamoto et al., 2008; Tanaka et al., 2008), photo-chemical deposition (Moriya et al., 2006) and electrodeposition (Scragg et al., 2009). Katagiri and co-workers have extensively investigated different properties of CZTS thin films prepared through sulfurization of precursors deposited by

electron beam evaporation (Katagiri et al., 1996; Katagiri et al., 1997; Katagiri et al., 2001a; Katagiri et al., 2001b; Kobayashi et al., 2005; Katagiri, 2005; Katagiri et al., 2003). Ito and Nakazawa reported, for the first time, the photovoltaic effect in a heterodiode structure with transparent conducting film of cadmium tin oxide and CZTS thin film. They reported an open-circuit voltage of 165 mV (Ito and Nakazawa, 1988). Katagiri et al. reported an efficiency of 6.77% for CZTS based solar cell having the structure Al/ZnO:Al/CdS/CZTS/Mo/glass (Katagiri et al., 2008). Todorov et al. reported the highest conversion efficiency of 9.66% in mixed sulfoselenide $[Cu_2ZnSn(S,Se)_4]$ device. They obtained a short-circuit current density of 36.4 mA/cm$^2$ (Todorov et al., 2010). In 2009, Moritake et al. reported the preparation of CZTS solar cell under non-vacuum condition (Moritake et al., 2009). Recently Krustok et al. reported the temperature dependence of cell parameters on $Cu_2ZnSn(Se_xS_{1-x})_4$ monograin solar cells (Krustrok et al., 2010).

CZTS, being an ideal candidate for absorber layer in thin film solar cells, the choice of an economically viable and user friendly deposition technique also is a pre-requisite for successfully achieving the mission of cost-effectiveness. Chemical spray pyrolysis [CSP] is a technique that caters to such demands. There are not many reports on preparation and characterization of sprayed CZTS thin films; however in 1996, Nakayama and Ito reported a two-step process to prepare stoichiometric CZTS films having kesterite structure. In this, CZTS was deposited on a glass substrate using spray technique which was followed by sulfurization at 550 °C (Nakayama and Ito, 1996). Madarasz et al. prepared CZTS thin films using the thermal decomposition of thiourea complexes of Cu(I), Zn(II), and Sn(II) chlorides (Madarasz et al., 2001). Kamoun et al. reported the preparation of CZTS thin films with kesterite structure through spray pyrolysis technique (Kamoun et al., 2007). XRD studies of these films indicated the presence of multiple phases. Very recently Kishore Kumar et al. reported preparation and characterization of spray pyrolysed CZTS thin films (Kishore Kumar et al., 2009a; Kishore Kumar et al., 2009b; Kishore Kumar et al., 2010). They reported the properties of the CZTS films deposited by varying substrate temperature, pH of the starting solution and concentrations of copper and thiourea salts.

Even though all these reports focus on deposition and characterization of CZTS thin films using spray pyrolysis, the effects of precursor variation on the properties of sprayed CZTS thin films have not been reported yet. Another novelty in our approach lies in p–n junction trials by using a cadmium free buffer layer. Nowadays lots of works are going on for the effective replacement of CdS. The motivation behind this is not only to eliminate toxic cadmium but also to improve light transmission in the blue wavelength region by using a material having band gap wider than that of CdS. Commendable variation in the properties of the films due to precursor variation and suc-

cessful junction trials with $In_2S_3$ buffer layer have been discussed in detail, in the present work.

## 2. Experimental details

CZTS films were deposited on cleaned soda lime glass substrates, using indigenously fabricated automated spray machine (Sebastian et al., 2009). These substrates were placed on a base plate (stainless steel). Temperature of the substrate could be varied from room temperature to 673 K. During spray, temperature of the substrate was kept constant with an accuracy of ±5 K. The heater and the substrate along with the spray head were kept inside a chamber, provided with an exhaust fan for removing gaseous byproducts and vapors of the solvent.

In the present work, we used two different precursors for tin viz., stannous chloride $(SnCl_2)$ and stannic chloride $(SnCl_4)$. Aqueous solution containing cuprous chloride (0.02 M), zinc acetate (0.0125 M), stannous chloride $(SnCl_2)$/stannic chloride $(SnCl_4)$ (0.0125 M) and thiourea (0.15 M) was sprayed at a rate of 8 ml/min onto the substrate kept at 623 K using compressed air (pressure ∼1.5 bar) as the carrier gas. Concentration of thiourea was three times larger than that is required to maintain stoichiometry (0.05 M), to compensate for the loss of sulfur during pyrolysis. The samples prepared using stannous chloride and stannic chloride were named as A and B respectively.

Crystal structure of the films was analyzed using Rigaku (D. Max. C) X-ray diffractometer (employing Cu Kα line ($\lambda = 1.5405$ Å) and Ni filter) operated at 30 kV and 20 mA. Surface morphology of the films was studied employing Scanning Electron Microscope (SEM) (JEOL Model JSM-6390LV). Chemical composition of the films was determined with the help of Energy Dispersive X-ray Analysis (EDAX) system attached to the SEM. Thickness and roughness of the films were measured using stylus profiler (Dektak 6 M). Optical properties were studied using UV–Vis–NIR spectrophotometer (Jasco V-570 Model). Hall measurements were done using Ecopia (HMS-3000 model) Hall measurement system. The depth profiling of the junction was done using an X-ray Photoelectron Spectroscopy (XPS) ULVAC-PHI unit (Model-ESCA 5600 CIM) employing argon ion sputtering. Electrical studies were conducted using Keithley 236 Source Measure Unit (SMU).

For preparing p–n junctions, films of CZTS (samples A and B) were deposited over ITO coated glass substrates kept at 623 K which was followed by the deposition of $In_2S_3$ layer (In:S ratio 2:8) above it using CSP technique at the same substrate temperature. Silver electrodes of area 1 mm$^2$ were vacuum evaporated for top contact, at $2 \times 10^{-5}$ Torr. The cells were illuminated in the front wall mode using a tungsten halogen lamp, with an intensity of 100 mW/cm$^2$. The J–V characteristics of the cells were recorded using SMU with the help of Metric's Interactive Characterization Software (ICS).

## 3. Results and discussion

### 3.1. Composition analysis

EDAX measurements were done for analyzing the composition of the films (Table 1). Copper concentration was low in both the films as it was in the precursor solution. In most of the works reported in spray pyrolysed CZTS films the sulfur content is low (Kishore Kumar et al., 2009a; Kishore Kumar et al., 2009b; Kishore Kumar et al., 2010). Nakayama and Ito were able to increase the sulfur content in the spray deposited film to 48 at.% by adding 30 vol.% ethanol to the solvent (Nakayama and Ito, 1996). But we could deposit films in which the sulfur content was quite close to the stoichiometric value. It could be observed that the film B was nearly stoichiometric with Cu/(Zn + Sn) ratio of 0.914, Zn/Sn ratio of 0.875 and S/metal ratio of 1.01. But the composition of film A showed large deviation from stoichiometry. Chlorine was present in both the samples in same proportion, irrespective of the precursor solution chosen. Though the reason is quite obscure, we could observe that the Sn content in A was much higher than that of B.

### 3.2. Structural studies

X-ray diffractograms of films A and B are depicted in Fig. 1. Peaks corresponding to the (1 1 2), (2 0 0), (2 2 0), (3 1 2) planes of CZTS could be observed. These are characteristic of the 'kesterite' structure of CZTS. For both the films, preferential orientation was along the (1 1 2) direction. We can also see some peaks corresponding to the binary phase Cu$_x$S.

Crystallite size ($D$) was determined using Debye Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where $\lambda$ is the wavelength of Cu K$\alpha$ line, $\beta$ is the FWHM in radians and $\theta$ is the Bragg angle. Crystallite size (Table 2) increased from 18 nm to 35 nm when the precursor was changed from stannous to stannic.

From the XRD peaks, lattice constants were calculated. CZTS has tetragonal structure, so the lattice constants are calculated using the equation

$$\frac{4 \sin^2 \theta}{\lambda^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$
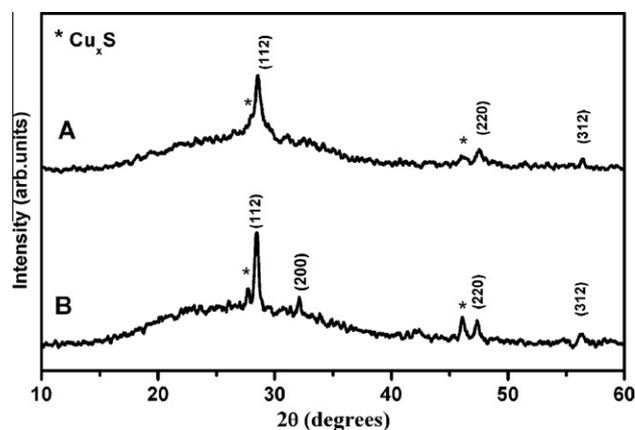


Fig. 1. XRD patterns of CZTS films A and B.

Table 2
FWHM and crystallite size of CZTS films deposited using various precursors.

| Sample name | FWHM (degrees) | Crystallite size (nm) |
|---|---|---|
| A | 0.45 | 18 |
| B | 0.23 | 35 |

where $h$, $k$ and $l$ are the Miller indices of the plane. The $2\theta$ values chosen for the calculation were 28.45° corresponding to (1 1 2) plane and 47.36° corresponding to (2 2 0) plane. The obtained lattice constants were $a = 0.5424$ nm and $c = 1.086$ nm. These values are in good agreement with the reported single crystal data, $a = 0.5427$ nm and $c = 1.0848$ nm.

### 3.3. Optical properties

Optical band gap of the samples were deduced from the plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$, by extrapolating the straight line portion of the graph in the high absorption regime (Fig. 2), where $\alpha$ and $h\upsilon$ are absorption coefficient and photon energy.

It was observed that film A exhibited much lower band gap ($\sim$1.30 eV) as compared to film B ($\sim$1.50 eV). The lower band gap of sample A may be due to the deviation of chemical composition from stoichiometry (Tanaka et al., 2008). But the band gap of sample B is fairly close to the optimum value for a solar cell absorber. The absorption coefficient in the visible region was larger than $10^4$ cm$^{-1}$. These values are in good agreement with the reported values (Moriya et al.,

Table 1
Chemical compositions of CZTS films deposited using various precursors.

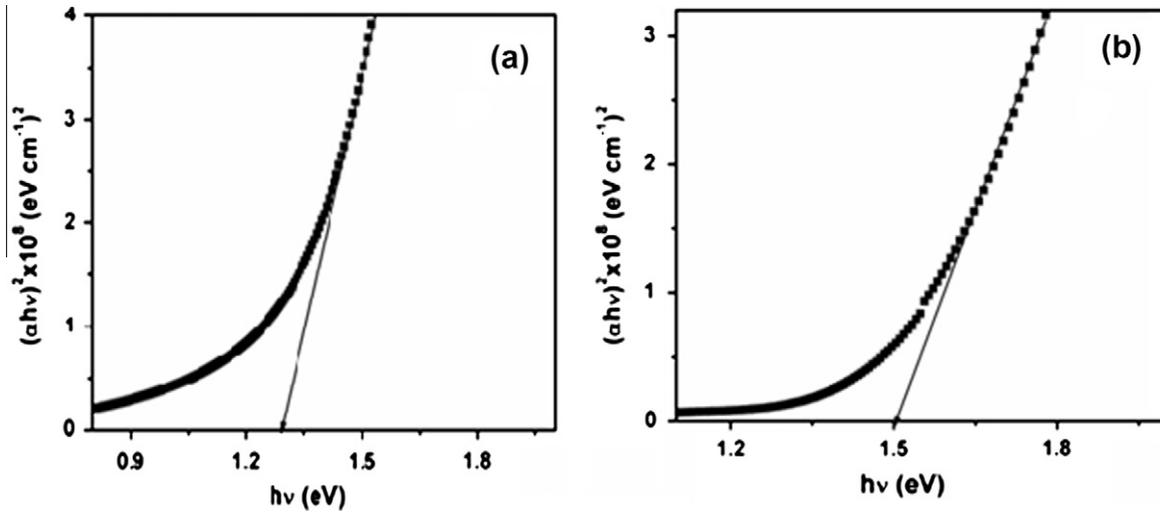| Sample name | Elemental composition (in at.%) | | | | | Cu/(Zn + Sn) | Zn/Sn | S/metal |
|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Sn | S | Cl | | | |
| A | 22.4 | 7.4 | 19.5 | 47.9 | 2.8 | 0.83 | 0.38 | 0.97 |
| B | 23.1 | 11.8 | 13.5 | 48.9 | 2.6 | 0.91 | 0.88 | 1.01 |

Fig. 2. Absorption spectra of CZTS films prepared using different precursors. (a) film A and (b) film B.

2007; Tanaka et al., 2007). No signature of $Cu_xS$ phase could be obtained from the absorption spectra.

### 3.4. Surface morphology

Fig. 3 depicts the SEM images of CZTS thin films A and B. The micrographs indicate that there are no well-defined grains in the film A. The grains are larger and densely packed in film B indicating that grain growth is enhanced due to a change in precursor solution. The grain size values (1–2 μm) match perfectly well with the reported values (Kishore Kumar et al., 2009a).

### 3.5. Electrical properties

From device point of view, it is highly warranted to have a better insight into the variation in carrier concentration, mobility and sheet resistance of the samples with variation in precursor. Room temperature resistivity of the samples was calculated using two probe method. The values obtained were $1.38 \times 10^{-1}\ \Omega\,cm$ and $5.2 \times 10^{-3}\ \Omega\,cm$ for films A and B respectively. We observe that, the resistivity decreases by two orders of magnitude just by changing the precursor from stannous to stannic. There have been reports about controlling the resistivity by varying substrate temperature (Kishore Kumar et al., 2009a). However, variation in resistivity by this order, solely due to a change in precursor, has not been reported earlier.

Hall measurements (Table 3) were performed which indicated that sample B was far better in terms of carrier concentration and mobility, which is obviously higher than the values obtained for the other set of films. The resistivity values obtained from Hall measurement system using van der Pauw method were in good agreement with that obtained from two probe method. Positive value of Hall coefficient indicated that both samples were p-type. Thus
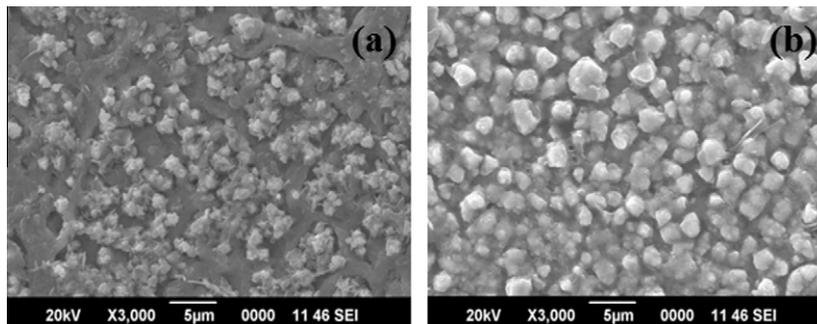


Fig. 3. SEM micrograph of CZTS films prepared using different precursors (a) film A (b) film B.

Table 3
Data obtained from hall measurement system for CZTS films A and B.

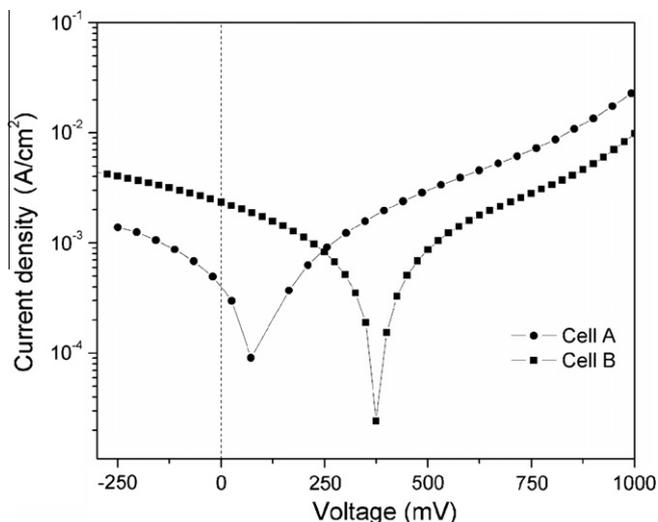| Sample name | Bulk carrier concentration (cm$^{-3}$) | Mobility (cm$^2$/V s) | Resistivity ($\Omega$ cm) | Average hall coefficient (cm$^3$/C) |
|---|---|---|---|---|
| A | $1.03 \times 10^{19}$ | 1.98 | $3.07 \times 10^{-1}$ | $6.06 \times 10^{-1}$ |
| B | $0.83 \times 10^{21}$ | 2.21 | $3.43 \times 10^{-3}$ | $7.57 \times 10^{-3}$ |

Fig. 4. Semilogarithmic plot of the Illuminated *J–V* characteristics of the cell prepared using film A (Cell A) and film B (Cell B).

Table 4
Cell parameters of CZTS based solar cell deposited using various precursors.

| Cell using CZTS film | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) |
|---|---|---|
| A | 91 | 0.41 |
| B | 380 | 2.40 |

from the optical and electrical characterizations, stannic chloride was adjudged as the precursor which yielded samples with properties ideal for device purpose.

In order to ascertain our observations that stannic chloride based CZTS films are candidates with ideal properties for absorber layer, junctions were fabricated. In$_2$S$_3$ was chosen as the buffer layer for cell trials with films A and B. For the cells prepared using A, the junction was quite good but it is sensitivity to light was negligible whereas for cells prepared using B, we got an open-circuit voltage ($V_{oc}$) of 380 mV and short-circuit current density ($J_{sc}$) of 2.4 mA/cm$^2$. The *J–V* curves under illumination, for cells prepared using A and B are shown in Fig. 4. Even though the carrier concentration is quite commendable, mobility is quite low as compared to reported values (Jun et al., 2006; Tanaka et al., 2005). This might be the reason for the low value of $J_{sc}$. For comparison, the $V_{oc}$ and $J_{sc}$ values obtained for both the junctions have been tabulated in Table 4.

From the XPS depth profiling of the junction (Fig. 5), the binding energy values obtained for Cu $2p_{1/2}$, Cu $2p_{3/2}$, Zn $2p_{3/2}$, Sn $3d_{3/2}$, Sn $3d_{5/2}$ and S $2p_{1/2}$ electrons were 952, 933, 1022, 495, 487 and 162 eV respectively, which matches closely with the values reported (Zhang et al., 2008). The atomic concentration of Cu, Zn, Sn and S obtained was in agreement with that obtained from EDAX measurements. Binding energies of indium indicated the formation of indium sulfide (444.9 and 452.9 eV for In3 $d_{5/2}$ and In3 $d_{3/2}$, respectively). It could be observed that Cu has diffused into the In$_2$S$_3$ layer which may be due to the high diffusion coefficient of Cu (Djessas et al., 2004). Due to this diffusion there is a gradient in concentration of Cu towards the junction which helps in the formation of resistive layer near the junction and a more conducting
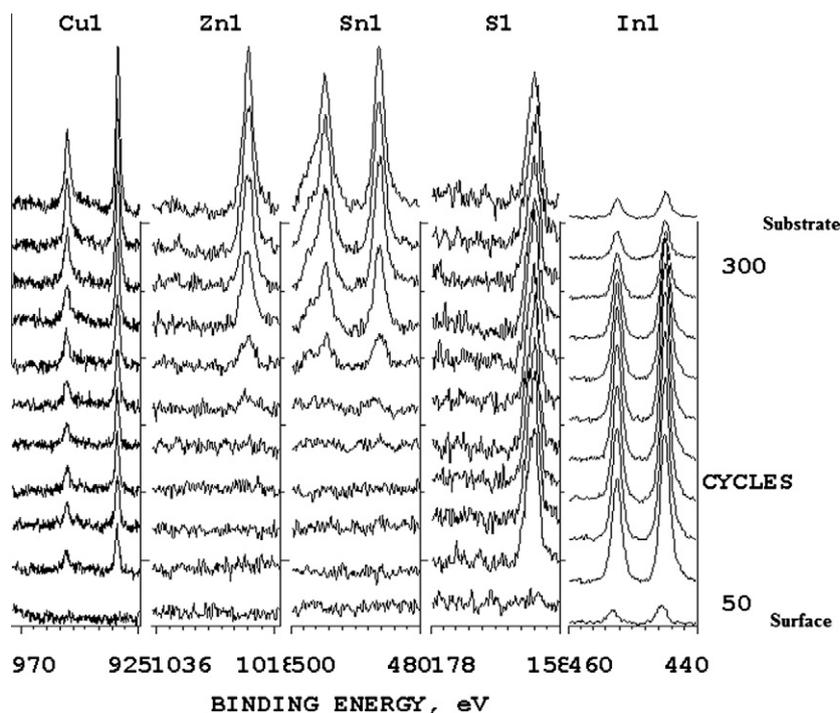


Fig. 5. XPS depth profile of the Cu$_2$ZnSnS$_4$–In$_2$S$_3$ junction.

layer near the collection electrode. Resistive layer near the junction is useful to reduce the leakage current.

## 4. Conclusions

The present work gives a clear idea on the control of structural and opto-electronic properties of spray deposited CZTS thin films through the choice of precursor. Ranging from improvement in crystallinity to enhancing the conductivity and mobility, we could conclusively prove that the choice of stannic chloride as precursor, yielded films with the desired properties to be used as absorber layer in solar cells. This really points out the capability of CSP technique in modifying the opto-electronic properties of semiconductor thin films making it more suitable for photovoltaic applications. We could substantiate our findings through p–n junction trials; here we used $In_2S_3$ as the buffer layer. We could obtain an open-circuit voltage of 380 mV and a short-circuit current density of 2.4 mA/cm$^2$.

## Acknowledgements

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