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BRIEF COMMUNICATION

Investigating the properties of tin-oxide thin film developed by sputtering process for perovskite solar cells

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Abstract

Tin oxide (SnO_2) nano-crystalline thin films were deposited on silicon and glass substrates at room temperature by sputtering at a constant power of 30 W and different working pressure of 10, 7, and 5 mTorr. Surface morphology, electrical and optical properties of the films were investigated to optimise the deposition condition of the films as electron transport layer (ETL) for high-power conversion efficiency perovskite solar cells. The films were characterized by scanning electron microscopy (SEM), UV–Vis–NIR Spectrophotometer, and Four-point probe. SnO_2 films obtained at working pressure of 10 mTorr exhibited uniform surface morphology with high light transmittance (90%) and conductivity (4 S/m). These sputtered SnO_2 films appeared to have shown promising properties as ETL for PSC, and further investigation is justified to establish the optimal fabrication parameters and resulting energy conversion efficiency.

Keywords Sputtering · Tin oxide · Electron transport layer · Thin films · SEM · Perovskite solar cells

Introduction

Renewable energy sources, such as wind, hydro, solar, hydrogen, and bio, are free of pollution and afford great relief from the global warming threat posed by the excessive burning of fossil fuels (e.g., coal, oil, and gas). Solar energy is the most abundant of all energy resources for heat, light, and electricity generation through thermal power generators and solar cells [1, 2]. A solar cell converts solar radiation into electric power by a chemical or physical process called the photovoltaic (PV) effect. This technology is clean and green, and produces no greenhouse effect on the environment [3, 4]. Despite all these benefits, because of high manufacturing and installation cost, the usage of solar technology for power generation is only 1% [5].

The emergence of second-generation thin-film solar cells with less material and reduced weight of the PV cells developed using innovative manufacturing technologies, and the possible fabrication of tandem cells with reasonably high-power conversion efficiency (PCE) make them attractive in critical applications [6]. The third-generation solar cells are based on semiconducting organic, inorganic, or hybrids including one of the highly promising perovskite solar cells (PSCs). The operation of the PSCs under direct solar energy involves electron and hole generation by light absorption of the perovskite material, charge separation into opposite sides, and collection of charge to the output circuit. The perovskite solar cell involves an organic absorber of perovskite structure, a p-type hole transport layer (HTL), and an n-type electron transport layer (ETL) of metal-oxide thin film [7]. The PSC consists of regular or inverted architecture as seen in Fig. 1. The perovskite structure is stable and can significantly contribute to the effectiveness of the solar cell arrangement as an organic absorber.

The NREL-certified record efficiency of PSC is 25.7% [8], and further improvement can be achieved with a better understanding of device architectures and resulting PCE due to optimal processing conditions. Moreover, the manufacturing process of these cells is simpler and more

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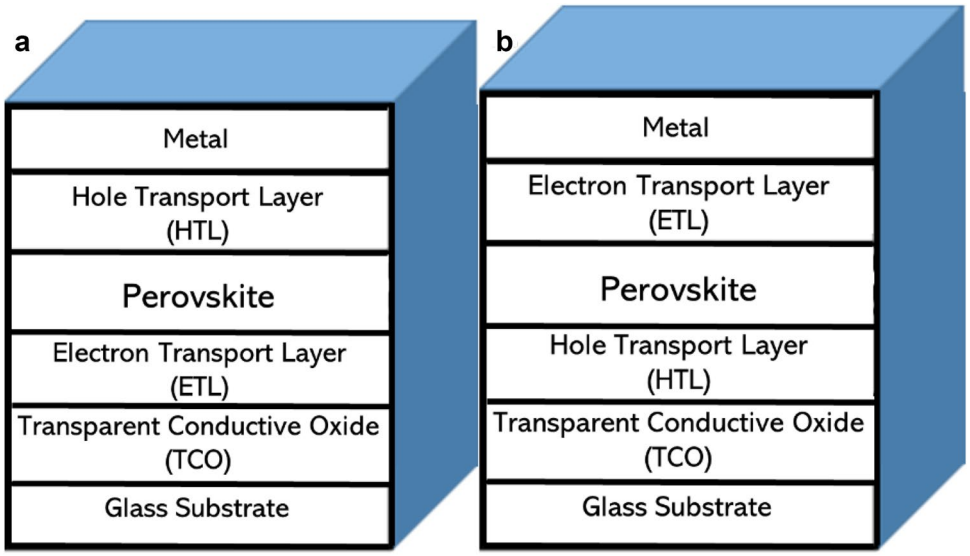

Fig. 1 Perovskite solar cell: **a** n–i–p planer regular architecture and **b** p–i–n inverted planer architecture

economical than that of the second- and third-generation solar cells [6, 9, 10]. The ETL and HTL play a vital part in achieving highly efficient devices with sustainability. However, regarding efficiency, ETLs suitable energy-level alignment improves charge separation and decrease recombination which produces better short-circuit current and higher fill factor [11]. The role of ETL is critical as they facilitate the photo-electron flow to the external circuit and deter short-circuiting by stopping the passage of the holes produced in the perovskite to the conductive electrode [9]. The ETL should be compact enough with excellent charge collection ability, pinhole-free, with a fitting bandgap and energy level, and good transparency [9]. The optimization of an n-type compact layer based on its ETL is critical to the efficiency enhancement of the PSC as it is responsible for electron conductivity/transport [7]. Still aiming to enhance the ETL, most research in recent years focused on investigating the consequence of ETL thickness and its feasible advancement strategy [12]. High resistance means thick ETL that opposes electron flow resulting in low PCE as the electrons have to travel longer distance to reach the top electrode. This was demonstrated by Jeyakumar et al. with titanium Oxide (TiO_2) ETL [13]. The cell series resistance will be very high if the ETL is too thick; subsequently, *Jsc* and Fill Factor of the cell reduce. Similarly, very-thin ETL thickness will encourage direct contact amid transparent conductive oxide (TCO) and perovskite resulting in carrier recombination and low hole-blocking efficiency. TiO_2 films, prepared by spray pyrolysis, were observed to have pinholes in ETL that resulted in the poor PCE of the PSCs [14]. The atomic layer deposition (ALD) technique provided a conformal, homogenous, and compact ETL with mesoscopic structure, having porous metal-oxide support on the films, and fewer pin holes that upsurged the PCE of the PSC from 4 to 13.6% [15]. However, despite the advantage of the mesoscopic structure, the TiO_2 requires a high temperature (more than 450 °C) to process, which makes the operation hazardous and cost-intensive [16]. The last record (2022) of PSC has been found using SnO_2 quantum dot as ETL could be more efficient with a better-aligned conduction band (see Fig. 2b), higher carrier mobility, and high operational stability [17]. This is attributed more to its barrier-free active conformation, and thus, ions are not restricted from reaching the perovskite. Thus, tin oxide (SnO_2) with better optical and electrical features that can be processed a low temperature could be a better alternative to TiO_2 thin film as ETL in PSCs [16], as shown in Fig. 2a. In terms of stability of PSC device, SnO_2 as ETL is higher than TiO_2 and ZnO due to wide bandgap (see Fig. 2c and d) with absorbing fewer UV [9, 18].

SnO_2 is an amphoteric compound of an inorganic composition having a cassiterite mineral form and exhibits good optical and electrical properties [19]. It is also mechanically hard, atmospherically stable, chemically inert, and high-temperature resistant [20]. Various studies revealed that monocrystalline film of SnO_2 is more than 18% hysteresis-free in PSC device [21]. Under forward and reverse voltage measurements, the PSCs with SnO_2 ETL on best performance attained 14.82% and 17.21% PCE, respectively [22, 23]. The fabrication of SnO_2 as an ETL for PSC produces an average PCE of 19.2–20.23% with mitigated hysteresis [21]. Jiang et al. [16] confirmed that introducing SnO_2 instead of fullerene or TiO_2 as an ETL in PSCs will mitigate interface charge accumulations and improve the transmission of charge generated in the perovskite absorber to the ETL due to its high electron mobility and conduction band as earlier reported by Correa and Baena et al. [18]. SnO_2 observes adequate energy-level alignment with the perovskite, exhibits

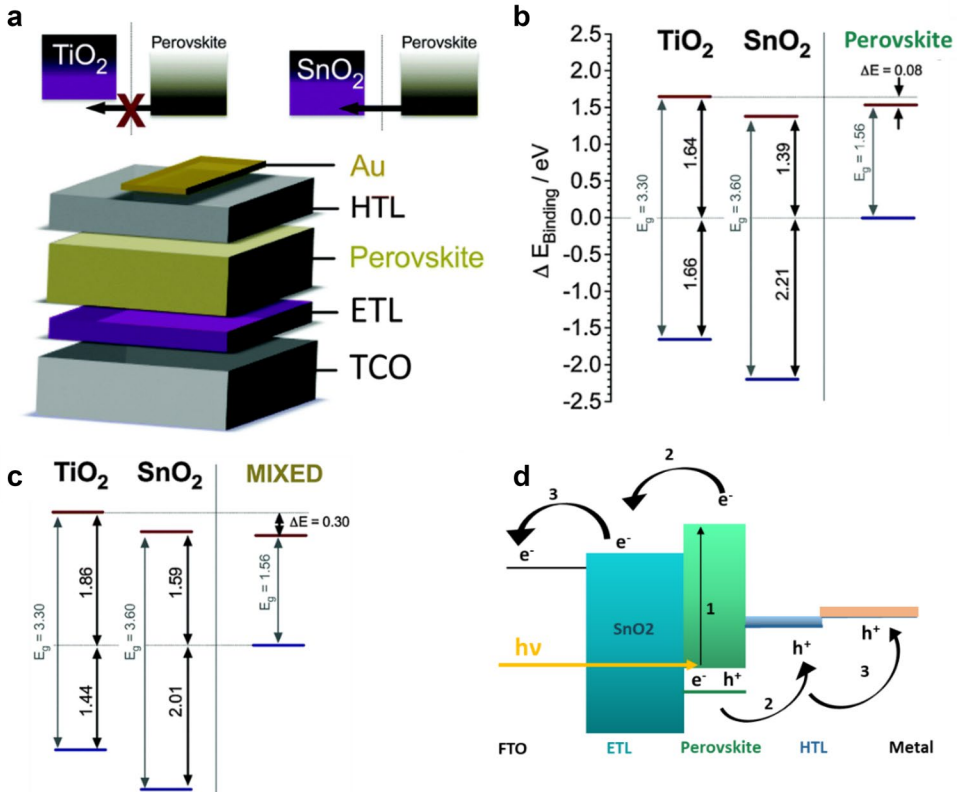

Fig. 2 **a** TiO_2 and SnO_2 energy levels, **b** electron injection potentials, **c** band-gap position of SnO_2, and **d** band-gap position [17, 18]

a wide bandgap of 3.6–4.0 eV [18] and an initial low resistivity and high conductivity (electron mobility) due to the presence of oxygen valences that produces carriers, and initiates a 15–150 meV donor platform/level [24]. SnO_2 as ETL induces low current loss as it absorbs light with higher energies than the bandgap [25]. SnO_2 films possess good transparency with ultimate absorption which corresponds to electron excitation from the valence band to the conduction band that determines the nature and value of the optical bandgap. Therefore, to ensure good passage of light through the ETL the film thickness of the ETL should be optimised to the best transparent quality alongside the reflectivity.

In general, this paper chose SnO_2 for its low cost, better band-gap energy alignment with perovskite, and good electrical and optical properties to enhance the PCE of the PSCs. In addition, SnO_2 is a promising material due to its low-temperature processing [26] in comparison to TiO_2 [16]. This research study examined properties of SnO_2 films deposited at different sputter pressure and room temperate by magnetron sputtering (see Fig. 3) for optimisation of the perovskite solar cell. Sputtering process allows

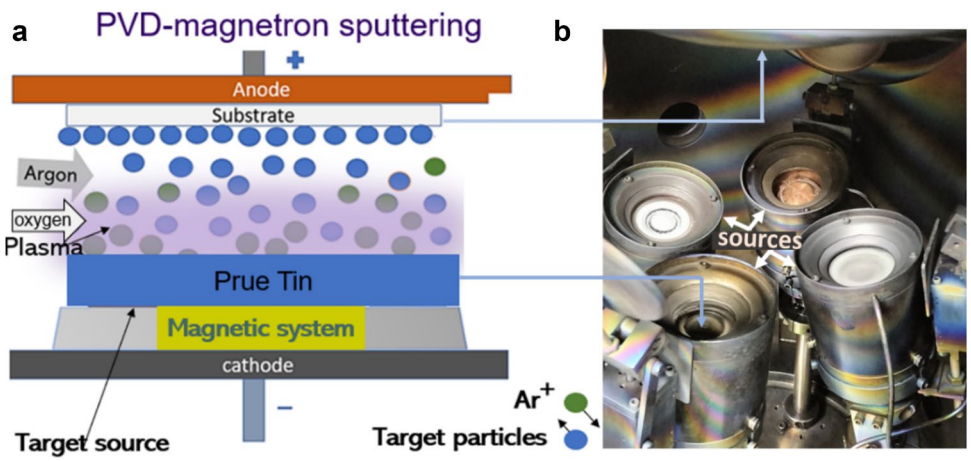

Fig. 3 **a** Magnetron sputtering process and **b** the internal view of the chamber

a controlled rate of film deposition, exceptional high film adhesion on substrates, outstanding film homogeneity on a large area, and good step coverage.

SnO_2 thin-film preparation

Sputtering is a physical vapour deposition technique that involves high energy (> 100 eV) ions (usually inert gas such as argon) to erode atoms on the surface of a target material. The ejected atoms must move freely toward the substrate. Sputtering occurs in vacuum to sustain high ion energies (plasma) and deter excess collisions of atom gas [27]. During the process, the gas atoms travel a mean free path (MFP) without any collision. The MFP fluctuates with pressure and is critical to unconstrained movement in the gas.

Magnetron sputtering involves a plasma discharge, confined, and sustained by a powerful field of magnet and secondary electrons to the area near the target plate. KJL PVD 75 is a conventional planar DC magnetron-sputtering machine that was used to prepare SnO_2 thin films onto glass and silicon substrates at different sputtering pressures and constant power deposition time and temperature. It has a cryogenic pump, reactive gas control system, and four HV magnetron-sputtering sources with RF DC and pulsed-DC power supplies. A circular flat disc of pure tin (99.9%) was used as the target material with a mixture of argon and oxygen as the working gas. The chamber was evacuated by the cryogenic pump with the sputter pressure monitored continuously using a Pirani and Penning pressure gauge. Three depositions were observed as the parameters are presented in Table 1.

Table 1 Parameters used in magnetron-sputtering process for SnO_2 thin-film fabrication

Common parameters			
Target material		Pure tin	
Target power (Watt)		30	
Deposition time (min)		60	
Ar/O_2 ratio		80:20	
Gas flowrate (cm^3/s)		11.5/2.3	
Substrate spin (rpm)		10	
Substrate Temp (°C)		25	
Variable parameters	Sample one (S1)	Sample two (S2)	Sample three (S3)
Base pressure (mTorr)	1.0×10^{-7}	1.0×10^{-7}	3.0×10^{-7}
Substrate	Glass and silicon	Glass	Glass
Working pressure (mTorr)	10	7	5

Characterization

The fabricated SnO_2 thin film was examined and analysed for transmittance and reflectance using a UV–Vis spectrophotometer, surface morphology using scanning electron microscopy (SEM), and electrical resistance and conductivity using a KeithLink four-point probe having constant probe diameter of 81 µm and probe spacing of 1.6 µm. The obtained results were compared with an optimal model for the application of PSC by Ref. [8].

Surface morphology

The surface morphology of the SnO_2 thin films on the silicon wafer and glass substrate was studied by observing SEM images captured using the TESCAN MIRA3 microscope. Figure 4 shows the surface feature of SnO_2 film deposited on silicon and glass substrates at working pressure of 10 mTorr. Apparently, at lower magnification, the surface looks quite smooth (see Fig. 4a and b), though a closer look at higher magnification shows vivid cracks that scatter incident light, thus decreasing light transmittance. On the other hand, instead of cracks, SnO_2 film deposited on glass substrate (see Fig. 4c and d) at 10 mTorr working pressure suffers from burnt grains like solid blisters that are irregular in size and distribution and is attributed to high scanning beam intensity from Tescan Mira. The morphology of the SnO_2 thin film on the glass substrates was further studied by depositing the SnO_2 at lower working pressure: 5 and 7 mTorr. The grains on the surface are smaller and more uniformly distributed films were created, as shown in Fig. 4g and h.

Film thickness and roughness

Film thickness and surface roughness were measured using stylus profilometer and atomic force microscopy (AFM), respectively, as shown in Table 2. The film thickness significantly decreases, whereas the surface roughness of the films slightly increases with increasing the working pressure from 5 to 10 mTorr. There is an optimum film thickness of ETL for high PCE perovskite solar cells, whereas the higher the surface roughness of the film, the higher the scattering loss of the incident light resulting in lower light transmittance. Therefore, there is a trade-off between the film thickness and the surface roughness of the SnO_2 film for optimum performance of PSCs.

Electrical properties

The electrical conductivity and resistance of the deposited SnO_2 films deposited at 10 and 7 mTorr (4 S/m) was found to be slightly higher than the film deposited at 5 mTorr (3

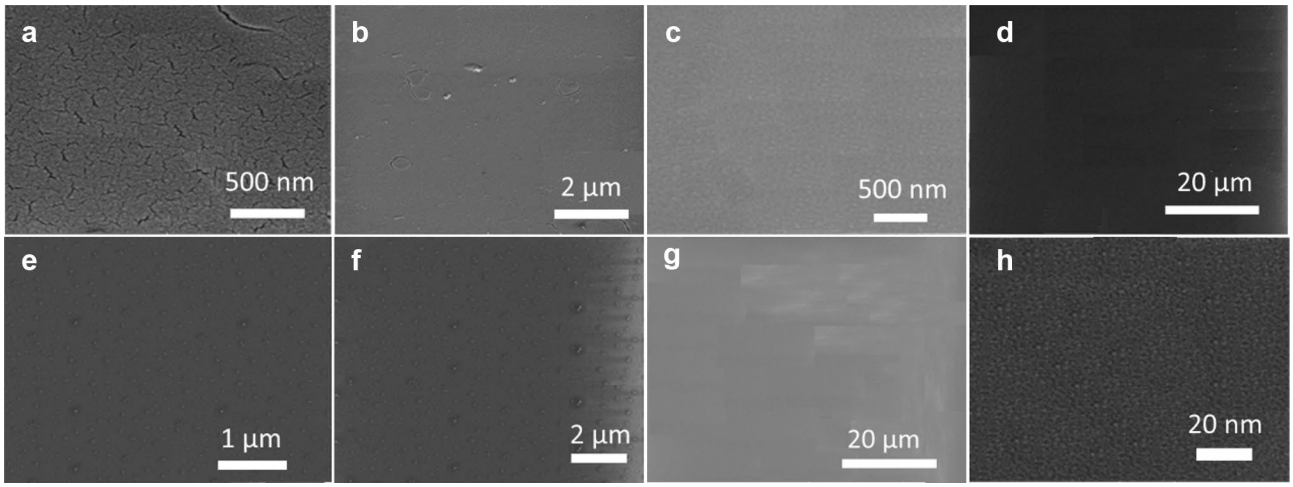

Fig. 4 SEM high and low magnification images of SnO_2 film deposited on silicon substrate (**a** and **b**) at 10 mTorr, and glass substrate (**c**, **d**), (**g**, **h**), and (**e**, **f**) at 10 and 7 and 5 mTorr working pressure, respectively

Table 2 Measured average film thickness, average surface roughness (Ra), and electrical conductivity (σ) at different sputter pressure (5, 7, 10 mTorr)

Samples	Pressure (mTorr)	Substrate	Thickness (nm)	Ra (nm)	σ (S/m)
S1	10	Silicon	58	2.00	–
		Glass	60	2.00	4
S2	7	Glass	72	1.85	4
S3	5	Glass	99	1.56	3

S/m) (see Table 2). The surface resistance and average resistance of the films at the different pressures (5, 7, 10 mTorr) are presented in Fig. 5a. The absolute values of the resistance were quite constant with insignificant variation against the different sputter pressure. Thus, working pressure is not a precursor parameter to affect resistivity.

Optical properties

The transmittance and reflectance spectra of the deposited SnO_2 films on the glass substrate were measured using dual beam CARY 500 UV−Vis–NIR in the solar wavelength spectrum (300 nm and 2500 nm), as shown in Fig. 5b. Only S1 maintained a close range of 90% transmittance and low reflectance, but the transmittance of the remaining two samples (S2 and S3) is much lower than this value (see Fig. 5b). From literature, common thickness used for ETL in PSCs was about 60 nm [28] and this value coincides with the SnO_2 film thickness of S1 (60 nm) with high transmittance that is useful for enhancing the PCE of the PCSs [18].

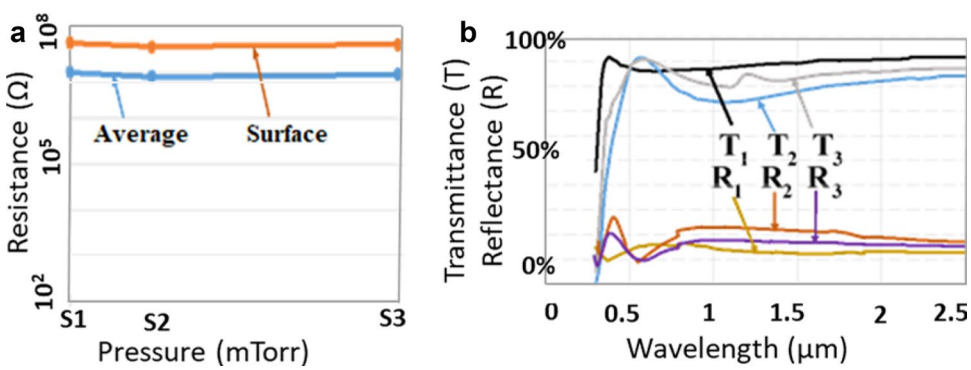

Fig. 5 **a** Average and surface electrical resistance at different pressure (10, 7, 5 mTorr for the individual samples), and **b** transmittance (T) and reflectance (R) of the films at different wavelength

Summary

From the focus on the ETL, SnO_2 thin films were fabricated on silicon and glass substrates for perovskite solar cells (PSCs) by magnetron sputtering at working pressure of 5, 7, and 10 mTorr and constant power of 30 W. The results could be summarised as follows:

- SEM images show cracks on the film produced on a silicon wafer at 10 mTorr, and hence, further investigation at 7 and 5 mTorr working pressure was discarded. On the other hand, small dots or grains could be seen on films produced on glass substrate.
- The variation in the electrical resistance and conductivity (varied between 3 and 4 S/m) of the films sputtered at different pressure (10, 7, 5 mTorr) was found insignificant.
- The transmittance of the SnO_2 film sputtered at 10 mTorr was found to be much higher (nearly 90%), than that the films deposited at 5 mTorr (75%) and 7 mTorr (82%).

The optimization of the electrical and optical properties, and the surface morphology of the SnO_2 film are dependent on deposition parameters, such as power, pressure, and temperature. The current study strongly demonstrates the potential application of SnO_2 thin film deposited at 10 mTorr and 30 W power with thickness of 60 nm for PSCs to achieve higher light conversion efficiency. Thus, further investigation is recommended to establish the optimal fabrication parameters and resulting electrical and optical properties including homogeneity and quality of the films.

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Data availability The data that support the findings of this study are available from the first and corresponding author, Chijioke Raphael Onyeagba, upon reasonable request.

Declarations

Conflict of interest The authors declare no known competing financial interests or personal relationships that could influence the work reported in this article.

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