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# Effects of Sn doping content on the structure, morphology, optical and electrical properties of ITO thin films prepared by microwave-assisted spray pyrolysis

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Indium tin oxide (ITO) thin films with different SnO<sub>2</sub> doping contents (0–20 wt%) were successfully deposited via microwave-assisted spray pyrolysis. The structure, morphology, optical and electrical properties of the as-deposited films were systematically investigated. In contrast to the undoped In<sub>2</sub>O<sub>3</sub> film, which exhibits a (222) preferential orientation, the SnO<sub>2</sub>-doped ITO films shows a shifted preferential orientation toward (400) along with a reduced (400) diffraction intensity. This orientation change induces significant variations in crystal texture, surface morphology, film thickness, as well as optical and electrical properties. As the SnO<sub>2</sub> doping content increased from 0 to 20 wt%, the thickness of the prepared films decreased continuously, while the surface roughness, the resistance, resistivity, and carrier concentration first decreased significantly and then increased. Notably, the 10 wt% SnO<sub>2</sub>-doped ITO film achieved substantially enhanced surface morphology, optical and electrical properties. This film is composed of regular spherical particles with a crystallite size of 43 nm, a root-mean-square roughness of 5.27 nm, and a total thickness of 310.3 nm. Furthermore, it exhibited an 85.94% transmittance in the visible wavelength range relative to the quartz substrate, a band gap energy of 3.84 eV, a sheet resistance of 7.4 Ω sq<sup>-1</sup> of, and a resistivity of 1.9 × 10<sup>-4</sup> Ω cm, respectively. Compared with ITO films prepared by traditional spray pyrolysis or other method, this film possesses superior electrical conductivity while maintaining comparable optical transmittance. Thus, the ITO film doped with 10 wt% SnO<sub>2</sub> is well-suited for electronic applications, particularly those requiring high-performance transparent conductive electrodes.

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## 1 Introduction

Tin-doped indium oxide, commonly referred to as indium tin oxide (ITO), is a well-known transparent conducting oxide (TCO) material consisting of a composite of indium oxide (In<sub>2</sub>O<sub>3</sub>) and tin oxide (SnO<sub>2</sub>). ITO thin films exhibit excellent optoelectronic performance, featuring high optical transmittance (>80%) in the visible spectral region coupled with ultra-low electrical resistivity (10<sup>-2</sup> to 10<sup>-4</sup> Ω cm).<sup>1-3</sup> The high visible-light transmittance of ITO films stems from their wide band gap ( $E_g = 3.5\text{--}4.3$  eV) at room temperature, whereas their low resistivity is attributed to a high carrier concentration (in the range of 10<sup>19</sup> to 10<sup>21</sup> cm<sup>-3</sup>) induced by oxygen vacancies and Sn dopants.<sup>1,4,5</sup> Owing to this outstanding synergy of optical and electrical properties, ITO films have been widely employed as transparent conductive electrodes in the fabrication of various

optoelectronic devices, including liquid crystal displays, flat panel displays, solar cells, sensors, and light-emitting diodes.<sup>6-8</sup>

ITO thin films can be fabricated using various methods, including electron beam evaporation,<sup>6</sup> sputtering,<sup>7,9</sup> sol-gel,<sup>10</sup> atomic layer deposition,<sup>11</sup> and spray pyrolysis.<sup>1,4,12</sup> Among these approaches, the spray pyrolysis (SP) technique is widely adopted owing to its simple fabrication procedure, low production cost, facile control over doping levels, and feasibility for large-area deposition. The SP process involves spraying a precursor solution onto a preheated substrate, where the subsequent chemical reaction proceeds to form metal oxide films on the high-temperature substrate.<sup>13</sup>

The optoelectronic properties of thin films are highly sensitive to deposition-induced microstructure, crystallographic texture, surface morphology and defects, all governed by the deposition method and processing parameters. For SP, rapid and uniform heating of atomized droplets is essential for homogeneous solvent evaporation, precursor thermal decomposition, and subsequent particle growth on the substrate. Microwave heating achieves volumetric heating *via* electromagnetic-to-thermal energy conversion, penetrating droplets to heat them uniformly from inside and out.<sup>14-16,22,23</sup> Conventional heating by conduction and convection, by

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contrast, causes slow, inefficient energy transfer and large droplet temperature gradients. Microwave-assisted spray pyrolysis (MSP) thus achieves rapid, uniform heating, yielding thin films and particles with enhanced structural and morphological quality. This superior performance has been validated in the synthesis of polycrystalline  $\text{SnO}_2$  and  $\text{SnO}_2\text{:F}$  thin films,<sup>14,17</sup>  $\text{Ca}_3\text{Co}_4\text{O}_9$  films,<sup>18</sup> Pt/graphene films,<sup>19</sup>  $\text{CuO/Cu}_2\text{O}$  microspheres,<sup>15</sup> hollow  $\text{Al}_2\text{O}_3$  microspheres,<sup>16</sup>  $\text{NiFe}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  nanoparticles,<sup>20</sup>  $\text{CeO}_2$  nanoparticles.<sup>21</sup>

Leveraging the advantage of MSP, our previous work,<sup>22,23</sup> confirmed the feasibility of fabricating ITO thin films *via* this technique, which enables the rapid synthesis of ITO films with fundamental structural and optoelectronic properties. However, these preliminary studies focused solely on process feasibility and the effect of microwave heating temperature, without investigating the intrinsic correlation between Sn doping behavior and microwave heating characteristics, nor establishing the structure–performance relationship of MSP-prepared ITO films. As a systematic extension of this prior research, the present work comprehensively studies the effects of Sn doping content on the crystal structure, surface morphology, optical transmittance and electrical conductivity of MSP-fabricated ITO films. We target Sn doping content optimization to improve film quality and enhance the overall optoelectronic performance of ITO films. Specifically aiming to elucidate the regulatory mechanism of Sn doping content on the crystal structure of ITO films under microwave volumetric heating, establish a quantitative structure–optoelectrical performance relationship for MSP-synthesized ITO films, and clarify the mechanism underlying optoelectronic performance degradation at excessive Sn doping levels. Overall, this work advances the further development and practical application of MSP technology in the synthesis of transparent conductive thin films and the fabrication of related optoelectronic materials.

## 2 Experimental

### 2.1 Materials

0.05 M precursor solutions were prepared by dissolving indium(III) chloride tetrahydrate ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ) and tin(IV) chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) in deionized water, yielding  $[\text{SnO}_2]/$

$[\text{SnO}_2 + \text{In}_2\text{O}_3]$  mass ratios of 0, 5, 10, 15 and 20 wt% in the final ITO films, respectively. A small amount of hydrochloric acid ( $\text{HCl}$ , 2 mL  $\text{L}^{-1}$ ) was added to enhance the solubility of the precursor mixtures, and each solution was magnetically stirred at 60 °C for 30 min to ensure homogeneous mixing and prevent gelation of the metal salts.

Films were deposited on circular quartz substrates (14 mm diameter and 2 mm thickness). Prior to deposition, all substrates were ultrasonically cleaned in ethanol, acetone and deionized water for 10 min each, then dried with pressurized air.

### 2.2 Preparation process

Fig. 1 presents the schematic diagram of MSP for ITO thin films deposition on quartz substrates. The prepared precursor solution was loaded into an ultrasonic atomizer (Yunnan Institute of Electronic Industry, China) with a frequency of 1.7 MHz and a spray flow rate of 0.12  $\text{L h}^{-1}$ . The solution was ultrasonically atomized into tiny droplets, which were sprayed onto a pre-heated quartz substrate fixed at the center of a homemade tube-type microwave furnace (described in ref. 22 and 23), with a fixed spraying distance of 30 cm. Compressed air (0.25  $\text{m}^3 \text{h}^{-1}$ ) was used as the carrier gas for droplet delivery and oxidation. The substrate temperature was maintained at  $500 \pm 2$  °C *via* microwave heating (2.45 GHz, 1.5 kW), and the deposition time was fixed at 30 min. Acidic tail gas generated was absorbed by 3 M NaOH before emission.

After deposition, the as-prepared films were naturally cooled to room temperature, collected and sent for characterization and testing. Two replicate experiments were performed under the same deposition parameters, and the relative standard deviation (RSD) is provided in the SI.

### 2.3 Characterization

The crystal structure was characterized by a Rigaku X-ray diffraction meter (XRD, D/Max 2200) with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418$  Å). Surface morphology was observed by an Agilent atomic force microscopy (AFM, 5500 AFM/SPM), and film thickness was obtained from cross-sectional images using a Philips scanning electron microscope (SEM, XL-30E). Optical transmittance (300–900 nm) was measured with a Hitachi UV-

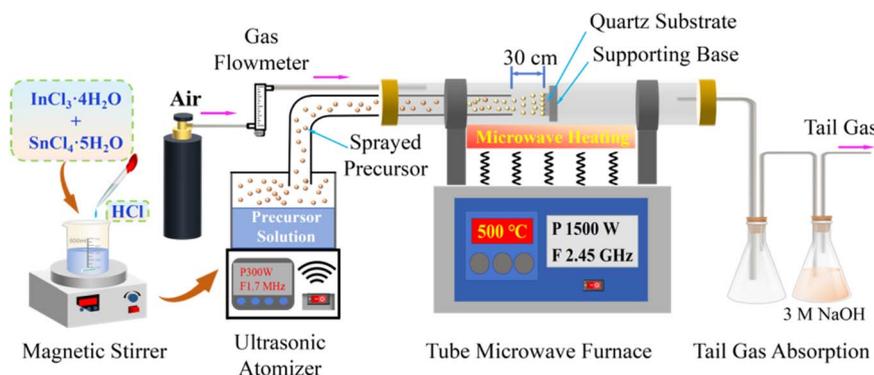


Fig. 1 Schematic diagram of microwave-assisted spray pyrolysis for preparing ITO thin films.



vis spectrophotometer (U-4100). Sheet resistance was tested using a ROOKO four-point probe (FT-341), and carrier concentration was determined *via* the van der Pauw method on a Semishare X3 Hall Effect Measurement System (TEKTRONIX, China).

## 3 Results and discussion

### 3.1 Structure

XRD patterns of the deposited thin films with different SnO<sub>2</sub> doping contents (0–20 wt%) are shown in Fig. 2. All films exhibit a cubic In<sub>2</sub>O<sub>3</sub> crystal structure (JCPDS PDF #71-2194), with no diffraction peaks corresponding to tin compounds. This indicates that all Sn<sup>4+</sup> ions incorporate into the In<sub>2</sub>O<sub>3</sub> lattice by substituting In<sup>3+</sup> ions, forming a single-phase solid solution of ITO. Two intensive diffraction peaks at  $2\theta = 30.6^\circ$  and  $35.5^\circ$  correspond to the (222) and (400) crystal planes of In<sub>2</sub>O<sub>3</sub>, respectively, but their intensities differ significantly. The intensity ratio  $I_{(400)}/I_{(222)}$  was used to evaluate the effect of SnO<sub>2</sub> content on film texture (Fig. 3). The undoped In<sub>2</sub>O<sub>3</sub> film is polycrystalline with a preferred (222) orientation, consistent with standard In<sub>2</sub>O<sub>3</sub> powder. In contrast, SnO<sub>2</sub>-doped films show a preferred (400) orientation, in agreement with previous reports on traditional spray pyrolysis.<sup>1,2,4</sup> With increasing SnO<sub>2</sub> content (5–20 wt%), the (400) peak intensity gradually decreases while the (222) intensity increases, reducing the  $I_{(400)}/I_{(222)}$  ratio from 7.9 to 1.4.

The above variations in diffraction peak intensity and preferred orientation can be well explained by the regulatory effect of SnO<sub>2</sub> doping on oxygen vacancies and lattice structure, which determines the preferred orientation of ITO films together with atomic mobility and high-energy atomic species.<sup>3,24–26</sup> In SnO<sub>2</sub>-doped In<sub>2</sub>O<sub>3</sub> films, Sn<sup>4+</sup> ions substitute In<sup>3+</sup> lattice sites and act as electron donors, inducing a higher density of oxygen vacancies.<sup>29</sup> These vacancies provide

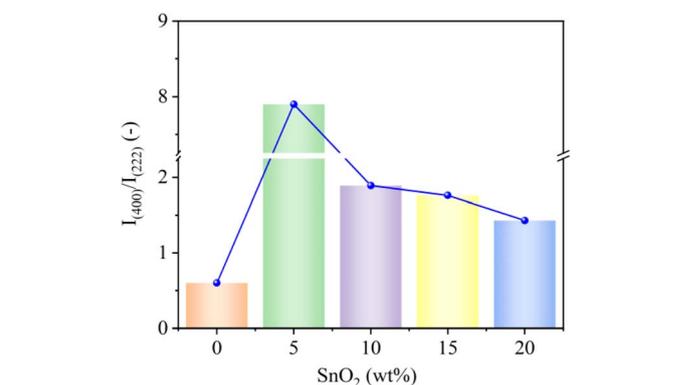


Fig. 3 The intensity ratio  $I_{(400)}/I_{(222)}$  for prepared ITO films with SnO<sub>2</sub> doping content.

additional active sites for ionic migration, enhancing film crystallinity and ionic mobility. Since oxygen vacancies preferentially form along the (400) crystal direction in SnO<sub>2</sub>-doped films, while (222) orientation prevails in pure In<sub>2</sub>O<sub>3</sub> films without such vacancy-induced growth promotion.<sup>3,24</sup> However, excessive SnO<sub>2</sub> doping releases more free electrons, inducing lattice disorders in the In<sub>2</sub>O<sub>3</sub> structure.<sup>25,26</sup> This disrupts the preferential growth of (400) orientation and causes competitive and random growth of (400) and (222) orientations, thereby resulting in the decreased diffraction intensity of the dominant (400) peak with further increasing SnO<sub>2</sub> content.

To further evaluate the preferred orientation, grain size and lattice strain, additional calculations were conducted based on the XRD data, as detailed below.<sup>8,12</sup>

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{(1/N)\sum_N I_{(hkl)}/I_{0(hkl)}} \quad (1)$$

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

$$\sigma = \frac{\beta \cos \theta}{4K} \quad (3)$$

where  $TC_{(hkl)}$ ,  $D$ , and  $\sigma$  denote the texture coefficient of the  $(hkl)$  plane, average grain size, and lattice strain, respectively.  $I$ ,  $I_0$  and  $N$  represent the measured diffraction intensity, standard reference intensity, and number of reflections, respectively. In addition,  $\lambda$ ,  $\theta$ , and  $\beta$  correspond to the X-ray wavelength (1.5405 Å for Cu K $\alpha$  radiation), diffraction angle, and full-width at half-maximum (FWHM) of the diffraction peak, respectively.

Table 1 presents the FWHM,  $TC_{(hkl)}$ ,  $D$ , and  $\sigma$  values of the prepared ITO films with different SnO<sub>2</sub> doping contents. FWHM decreases with increasing SnO<sub>2</sub> content, indicating improved ITO film crystallinity during MSP process, which originates from the synergistic effect of Sn<sup>4+</sup> substitutional doping and microwave volumetric heating. Increased SnO<sub>2</sub> content elevates oxygen vacancies, relieving lattice stress and enhancing microwave absorption efficiency.<sup>35</sup> Microwave heating reduces migration activation energy and facilitates atomic movement, promoting ordered grain growth,<sup>36,37</sup> and reducing defects and

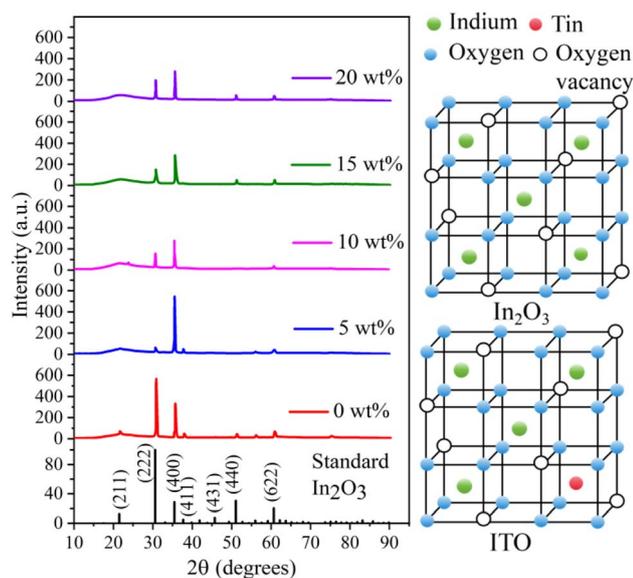


Fig. 2 XRD patterns and crystal structure of the deposited films with SnO<sub>2</sub> doping contents.



Table 1 Different parameters estimated from XRD studies for prepared films

| SnO <sub>2</sub> (wt%)                  | Preferred orientation | 2 $\theta$ (°) | FWHM (°) | Grain size $D$ (nm) | TC <sub>(hkl)</sub> | Microstrain $\sigma$ ( $\times 10^{-3}$ ) |
|---|-----------------------|----------------|----------|---------------------|---------------------|---|
| Standard In <sub>2</sub> O <sub>3</sub> | (222)                 | 30.58          | —        | —                   | —                   | —   |
| 0                                       | (222)                 | 30.85          | 0.266    | 44                  | 0.84                | 1.12                                      |
| 5                                       | (400)                 | 35.50          | 0.239    | 35                  | 2.56                | 0.99                                      |
| 10                                      | (400)                 | 35.52          | 0.218    | 43                  | 2.53                | 0.95                                      |
| 15                                      | (400)                 | 35.60          | 0.206    | 45                  | 2.37                | 0.86                                      |
| 20                                      | (400)                 | 35.60          | 0.205    | 46                  | 2.36                | 0.85                                      |

microstrain ( $\sigma$ ),<sup>8</sup> consequently narrowing FWHM, increasing crystallite size ( $D$ ), and enhancing overall crystallinity.

### 3.2 Morphology

The surface morphology and root-mean-square (RMS) roughness of the films were analyzed by AFM, as shown in Fig. 4. For undoped In<sub>2</sub>O<sub>3</sub> film, unevenly distributed triangular vertebral and spherical grains cover the substrate compactly. Grain

growth occurs along preferred nucleation centers, leading to mixed small and large grains, consistent with the high  $I_{(400)}/I_{(222)}$  ratio and microstrain in Table 1. This size heterogeneity results in a relatively rough surface with an RMS value of 22.9 nm. For SnO<sub>2</sub>-doped ITO films, increasing SnO<sub>2</sub> leads to more regular spherical grains and a flatter surface, with the lowest RMS value (5.27 nm) achieved at 10 wt% SnO<sub>2</sub>. However, further increasing SnO<sub>2</sub> to 20 wt% increases the RMS to

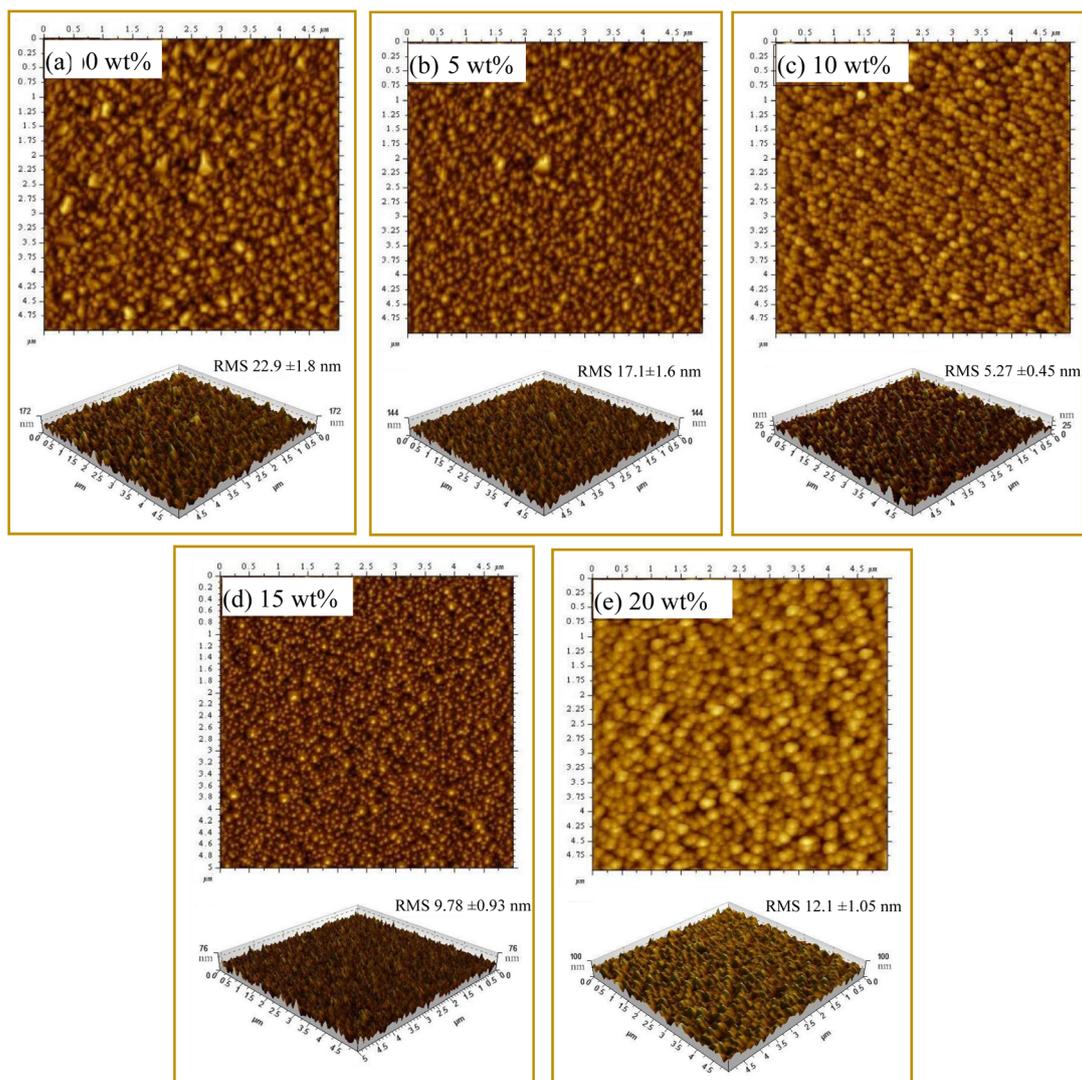


Fig. 4 AFM of the prepared ITO films with SnO<sub>2</sub> doping contents, (a) 0 wt% SnO<sub>2</sub>, (b) 5 wt% SnO<sub>2</sub>, (c) 10 wt% SnO<sub>2</sub>, (d) 15 wt% SnO<sub>2</sub>, and (e) 20 wt% SnO<sub>2</sub>.



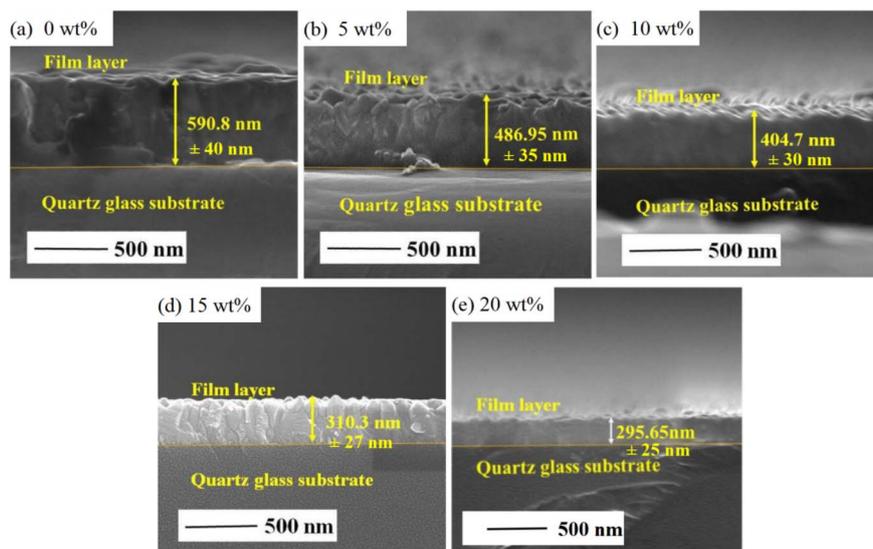


Fig. 5 SEM cross-section images of the prepared films with SnO<sub>2</sub> doping contents, (a) 0 wt% SnO<sub>2</sub>, (b) 5 wt% SnO<sub>2</sub>, (c) 10 wt% SnO<sub>2</sub>, (d) 15 wt% SnO<sub>2</sub>, and (e) 20 wt% SnO<sub>2</sub>.

12.1 nm. As shown in Table 1, SnO<sub>2</sub> doping improves film crystallinity and increases grain size. The improved crystallinity favors ordered film growth, while larger grains tend to roughen the surface.<sup>2,8</sup> Thus, the optimal 10 wt% SnO<sub>2</sub> doping yields film with the smoothest surfaces and lowest RMS.

Cross-sectional SEM micrographs and film thickness are shown in Fig. 5. Almost all films consist of densely packed columnar grains oriented perpendicularly to the substrate, with thickness decreasing significantly from 590.8 nm to 295.7 nm as SnO<sub>2</sub> content increases from 0 to 20 wt%. This is attributed to improved crystallinity (Fig. 2 and Table 1) and reduced (400) preferred orientation intensity (Fig. 3) with increasing SnO<sub>2</sub> doping. Due to the difference in ionic radii, Sn<sup>4+</sup> ions (0.69 Å) effectively substitute In<sup>3+</sup> ions (0.80 Å), filling intrinsic lacunas induced by volatilization of disordered regions in the In<sub>2</sub>O<sub>3</sub> matrix.<sup>1</sup> Enhanced crystallinity promotes ordered and well-oriented grains, forming a denser microstructure. Additionally, (400)-oriented grains exhibit higher momentum transfer efficiency and faster growth rates than (222)-oriented grains due

to surface energy differences.<sup>9,34</sup> As shown in Fig. 3, the decreasing  $I_{(400)}/I_{(222)}$  ratio with increasing SnO<sub>2</sub> content slows overall film growth. Thus, under identical deposition conditions, denser microstructure and slower growth rate lead to gradual thickness reduction with increasing SnO<sub>2</sub> doping.

### 3.3 Optical properties

Fig. 6 shows the transmittance spectra of films with different SnO<sub>2</sub> content, along with the bare quartz substrate spectrum. Key optical parameters, average transmittance in the visible region ( $T_{av}$ ),  $T_{av}$  ratio of film to substrate ( $T_{av-film}/T_{av-substrate}$ ), maximum visible transmittance ( $T_{max}$ ) and transmittance at 550 nm ( $T_{550\text{nm}}$ ), were derived from these spectra and are listed in Table 2.

As shown in Fig. 6 and Table 2, all films exhibit high transmittance in the visible range (380–780 nm), while transmittance degrades rapidly below 380 nm due to band-to-band transition absorption.<sup>7</sup> The absorption edge shift to shorter wavelength (Burstein–Moss shift), indicating a widened energy band gap ( $E_g$ ) with increasing SnO<sub>2</sub> dopant.<sup>1</sup>  $T_{av}$  increases with SnO<sub>2</sub> content up to 15 wt% and then decreases at 20 wt%. Notably, SnO<sub>2</sub>-doped ITO films show  $T_{av} > 85\%$  relative to the quartz substrate. Normalizing the substrate transmittance to 100% yields  $T_{av}$  up to  $>95\%$ , demonstrating high visible transparency critical for optical applications.

The energy band gap ( $E_g$ ) of the films was estimated using the Tauc's relation.<sup>7</sup>

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

where  $\alpha$  is the absorption coefficient,  $h\nu$  is the photon energy,  $A$  is a constant, and  $n = 1/2$  for direct band gaps. The absorption coefficient ( $\alpha$ ) was calculated as described previously.<sup>27</sup>

$$\alpha = \frac{1}{d_T} \ln\left(\frac{1}{T}\right) \quad (5)$$

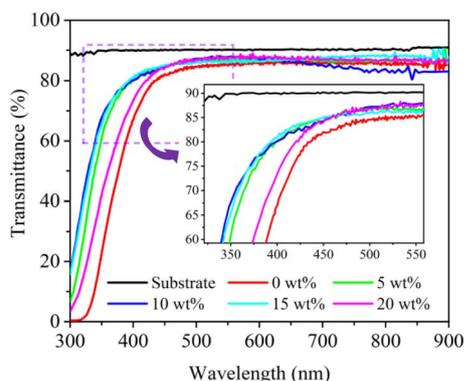
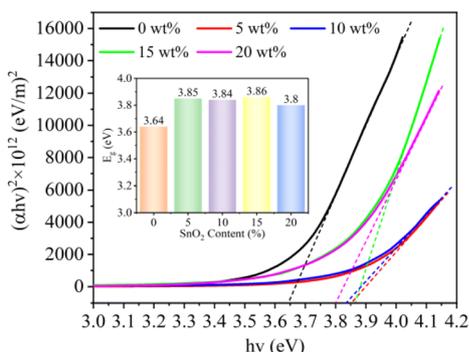


Fig. 6 Transmission spectra for the prepared films with SnO<sub>2</sub> doping contents.



Table 2 Optical property parameters of the prepared films

| Samples with different SnO <sub>2</sub> content (%) | $T_{av}$ (%) | $T_{av-film}/T_{av-substrate}$ (%) | $T_{max}$ (%) in the visible zone | Visible wavelength for $T_{max}$ (nm) | $T_{550\text{ nm}}$ |
|---|--------------|------------------------------------|-----------------------------------|---------------------------------------|---------------------|
| Quartz substrate                                    | 90.13        | 100                                | 90.41                             | 706                                   | 90.20               |
| 0   | 83.56        | 92.71                              | 86.59                             | 664                                   | 84.82               |
| 5   | 85.83        | 95.23                              | 88.41                             | 624                                   | 86.45               |
| 10  | 85.94        | 95.35                              | 88.02                             | 537                                   | 87.75               |
| 15  | 86.12        | 95.55                              | 88.41                             | 771                                   | 85.85               |
| 20  | 84.68        | 93.95                              | 89.00                             | 589                                   | 87.18               |

Fig. 7 Variation of  $(\alpha hv)^2$  versus  $hv$  for the prepared ITO films with SnO<sub>2</sub> doping contents and the inset shows the  $E_g$  values.

where  $d_T$  is the film thickness and  $T$  is the transmittance.

Fig. 7 presents plots of  $(\alpha hv)^2$  vs.  $hv$  for the prepared films.  $E_g$  values were obtained by extrapolating the linear regions of the  $(\alpha hv)^2$  vs.  $hv$  plots to the  $hv$  axis (inset of Fig. 7). The undoped In<sub>2</sub>O<sub>3</sub> film has an  $E_g$  of 3.64 eV, while the 5 wt% SnO<sub>2</sub>-doped ITO film shows a marked increase to 3.85 eV. This is consistent with previous reports that undoped (222)-oriented In<sub>2</sub>O<sub>3</sub> films prepared by traditional spray pyrolysis have  $E_g$  values of 3.53–3.68 eV.<sup>13</sup> With further increasing SnO<sub>2</sub> content,  $E_g$  decreases slightly, reaching 3.80 eV at 20 wt% SnO<sub>2</sub>.

The band gap shift stems from two competing mechanisms: widening induced by the Burstein–Moss effect and narrowing

caused by electron scattering.<sup>1,28</sup> Fig. 8 illustrates the mechanism by which varying SnO<sub>2</sub> contents affect the  $E_g$  of the ITO films. Compared to the undoped In<sub>2</sub>O<sub>3</sub> film, the  $E_g$  of SnO<sub>2</sub>-doped In<sub>2</sub>O<sub>3</sub> films increases markedly with increasing carrier concentration (Fig. 9c). This phenomenon can be attributed to the Burstein–Moss shift, which occurs when electrons fill higher energy states near the bottom of the conduction band.<sup>9</sup> In contrast, electron scattering is influenced by film crystallinity. As shown in Fig. 2, the improved crystallinity with increasing SnO<sub>2</sub> content corresponds to larger grain sizes and fewer grain boundaries, which reduces the excitation energy for intergranular electron migration, and thus induces  $E_g$  narrowing.<sup>29</sup> Consequently, the  $E_g$  of the films increases significantly initially and then fluctuates gradually with further increasing SnO<sub>2</sub> doping content, with higher carrier concentrations yielding larger  $E_g$  values.

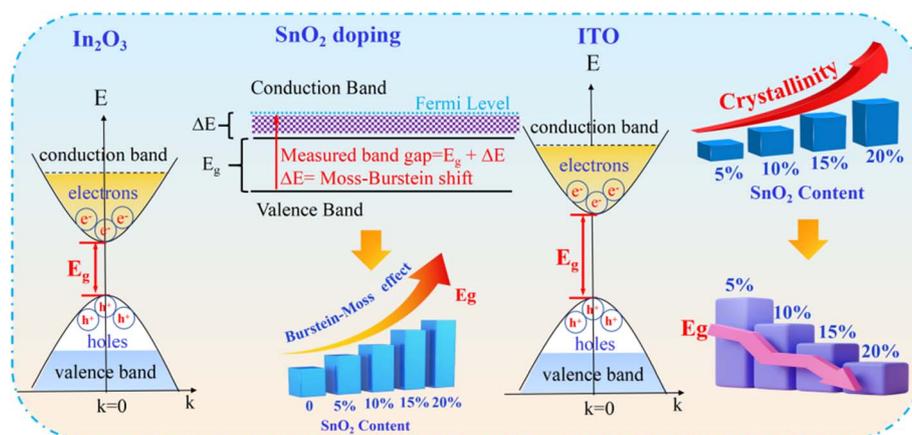
### 3.4 Electrical properties

The electrical conductivity of the films was characterized in terms of sheet resistance  $R_s$  and resistivity  $\rho$ , with their correlation expressed by the following equation:

$$\rho = R_s d_T \quad (6)$$

where  $d_T$  is the film thickness.

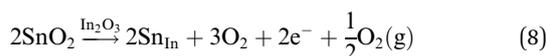
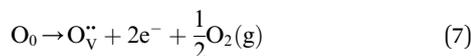
Fig. 9a and b show the variations in  $R_s$  and  $\rho$  of the films with different SnO<sub>2</sub> doping content. Evidently, SnO<sub>2</sub>-doped ITO films exhibits a remarkable conductivity enhancement relative to the

Fig. 8 The mechanism of the effects of varying content of SnO<sub>2</sub> on the optical property of ITO films.

undoped  $\text{In}_2\text{O}_3$  film.  $R_s$  plummeted from  $288.8 \Omega \text{ sq}^{-1}$  for the undoped sample to  $7.4 \Omega \text{ sq}^{-1}$  for the 10 wt%  $\text{SnO}_2$ -doped film (a  $\sim 39$ -fold reduction), while further increasing  $\text{SnO}_2$  to 20 wt% causes a slight rise in  $R_s$  to  $31.9 \Omega \text{ sq}^{-1}$ . Correspondingly,  $\rho$  decreases sharply and then slightly increases with increasing  $\text{SnO}_2$  content, with a minimum value of  $1.9 \times 10^{-4} \Omega \text{ cm}$  achieved for the 10 wt%  $\text{SnO}_2$ -doped ITO film.

Further analysis indicates that the changes in  $R_s$  and  $\rho$  are primarily governed by carrier concentration. Fig. 9c presents the carrier concentration ( $n$ ) and mobility ( $\mu$ ) of the ITO films as a function of  $\text{SnO}_2$  content. The  $n$  values increase drastically from  $6.2 \times 10^{18} \text{ cm}^{-3}$  (0 wt%  $\text{SnO}_2$ ) to  $1.46 \times 10^{21} \text{ cm}^{-3}$  (10 wt%  $\text{SnO}_2$ ), then decline to  $4.07 \times 10^{20} \text{ cm}^{-3}$  at 20 wt%  $\text{SnO}_2$ . In contrast,  $\mu$  shows an opposite trend. The undoped  $\text{In}_2\text{O}_3$  film exhibits a maximum  $\mu$  of  $59.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , whereas the 5–20 wt%  $\text{SnO}_2$ -doped ITO films shows slight  $\mu$  variations in the range of 14.4 to  $18.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

Hall effect measurements confirms the n-type conductivity of the prepared ITO films, with free electrons as the majority charge carriers. The variation in  $n$  (*i.e.*, free electrons density) arises from the synergistic effect of  $\text{SnO}_2$  doping and oxygen vacancies in the ITO lattice.<sup>5,7</sup> A doubly ionized oxygen vacancy ( $\text{O}_V^{\bullet\bullet}$ ) contributes two free electrons ( $2e^-$ ) to the conduction (eqn (7)), while the substitution of  $\text{In}^{3+}$  by  $\text{Sn}^{4+}$  in the cubic  $\text{In}_2\text{O}_3$  lattice ( $\text{Sn}_{\text{In}}$  substitution) donates one free electron (eqn (8)).



Compared with the undoped  $\text{In}_2\text{O}_3$  film, the significantly higher  $n$  of  $\text{SnO}_2$ -doped films stems from the combined effects of oxygen vacancies (eqn (7)) and  $\text{Sn}_{\text{In}}$  substitution (eqn (8)), thus leading to a dramatic reduction in  $R_s$  and  $\rho$  up to 10 wt%  $\text{SnO}_2$  doping. However, further increasing  $\text{SnO}_2$  above 10 wt% caused a decline in  $n$ , as the reduction in oxygen vacancies induced by increased surface roughness (Fig. 4) outweighs the  $\text{Sn}_{\text{In}}$  substitution from elevated  $\text{SnO}_2$  content.<sup>4</sup> A rough surface hinders the effective diffusion of Sn atoms into the  $\text{In}_2\text{O}_3$  lattice *via* grain boundaries or interstitial sites, which reduces the oxygen vacancies concentration generated by Sn diffusion,

subsequently decreasing free electrons and electrical conductivity. For  $\text{SnO}_2$ -doped ITO films, therefore, a more uniform surface correlates with higher electrical conductivity.

### 3.5 Comparison of optoelectrical properties

To comprehensively evaluate the suitability of the as-deposited films as transparent conductive oxide (TCO) materials for optoelectronic applications, the figure of merit  $\phi_{\text{TC}}$ , a parameter defined by the combined dependence on optical transmittance and electric resistivity, was calculated using Haacke's equation:<sup>30</sup>

$$\phi_{\text{TC}} = \frac{T^{10}}{R_s} \quad (9)$$

where  $T$  denotes optical transmittance and  $R_s$  is sheet resistance. Maximizing  $\phi_{\text{TC}}$  is practically significant, as it enables the rational selection of films with high transmittance while retaining low resistance.

Fig. 10 depicts the variation in  $\phi_{\text{TC}}$  of the films with  $\text{SnO}_2$  doping content. Incorporation of  $\text{Sn}^{4+}$  ions into the  $\text{In}_2\text{O}_3$  lattice leads to a dramatic rise in  $\phi_{\text{TC}}$ , with the maximum  $\phi_{\text{TC}}$  achieved for the 10 wt%  $\text{SnO}_2$ -doped ITO film, attributable to its low resistance and high transmittance. Further increasing  $\text{SnO}_2$  to 20 wt% induces a decline in  $\phi_{\text{TC}}$  due to the elevated resistance. Consequently, 10 wt%  $\text{SnO}_2$  is the optimal doping concentration for the ITO films, yielding a favorable balance of high optical transmittance and low electrical resistance.

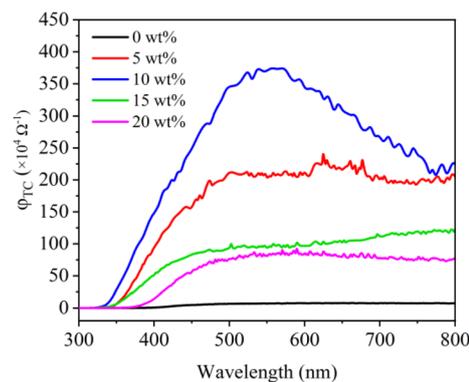


Fig. 10 Figure of merit of the prepared films with  $\text{SnO}_2$  doping contents.

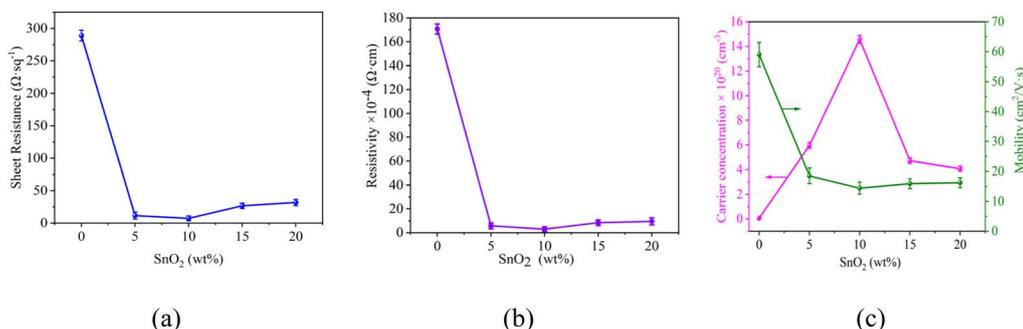


Fig. 9 (a) Sheet resistance, (b) resistivity, and (c) carrier concentration and mobility of the prepared films with  $\text{SnO}_2$  doping contents.





Table 3 Optoelectrical properties of ITO films prepared by different methods

| Methods                                      | Experimental conditions   | Optimized doping content      | Film thickness (nm) | $E_g$ (eV) | $T_{av}$ (wavelength range) | $R_s$ ( $\Omega$ sq $^{-1}$ ) | $\rho$ ( $\times 10^{-4}$ $\Omega$ cm) | Ref.      |
|--|---|-------------------------------|---------------------|------------|-----------------------------|-------------------------------|--|-----------|
| Microwave-assisted spray pyrolysis           | Precursor: 0.05 M (InCl <sub>3</sub> + SnCl <sub>4</sub> ), temperature: 773 K, microwave frequency: 2.45 GHz, time: 30 min, substrate: quartz, spraying distance: 30 cm  | 10 wt% of SnO <sub>2</sub>    | 296–591             | 3.84       | 95.35% (380–780 nm)         | 7.4                           | 1.9                                    | This work |
| Traditional spray pyrolysis                  | Precursor solution: InCl <sub>3</sub> + SnCl <sub>2</sub> , temperature: 723–773 K, substrate: glass, spraying distance: 45 cm  | 5 wt% of Sn                   | 300                 | —          | —                           | —                             | 3.3                                    | 1         |
| Traditional spray pyrolysis                  | Precursor solution: 6.25–37.5 mM (InCl <sub>3</sub> + SnCl <sub>4</sub> ), temperature: 773 K, substrate: glass, spraying distance: 28 cm   | 5 wt% of Sn                   | 135–205             | —          | 94.4% (380–780 nm)          | 132                           | 27.1                                   | 12        |
| Traditional spray pyrolysis                  | Precursor solution: InCl <sub>3</sub> + SnCl <sub>4</sub> , temperature: 753 K and 793 K, substrate: Corning 7059 glass   | 0.023 at% of Sn               | —                   | 3.46       | 80–90% (380–780 nm)         | 26.6                          | 14.5                                   | 4         |
| Traditional d.c. magnetron sputtering        | Target: In <sub>2</sub> O <sub>3</sub> -SnO <sub>2</sub> (90 : 10), temperature: 473 K, sputtering gas: Ar, working pressure: (4–15) $\times 10^{-2}$ torr, time: 20 min, target distance: 52 mm                        | 10 wt% of SnO <sub>2</sub>    | 110                 | 3.87       | 84.7% (380–780 nm)          | —                             | 37                                     | 7         |
| Microwave-enhanced d.c. magnetron sputtering | Target: In-Sn (90 : 10), oxygen partial pressure: $3.8-11.7 \times 10^{-4}$ mbar, substrate: glass, spraying distance: 122 mm   | 10 wt% Sn                     | 103–106             | 3.84       | 85% (1550 nm)               | —                             | 22                                     | 31        |
| Plasma enhanced atomic layer deposition      | Precursor: Cyclopentadienyl indium and tetrakis(dimethylamino)tin with SnO <sub>2</sub> -to-In <sub>2</sub> O <sub>3</sub> of 0 to 20%, temperature: 523 K, plasma power: 1500 and 3000 W, substrate: Si(100) and glass | 1.6 at% of Sn                 | —                   | 3.8        | 89% (380–780 nm)            | —                             | 2.9                                    | 11        |
| Sol-gel                                      | Precursor sol: 0.1 M In(NO <sub>3</sub> ) <sub>3</sub> + 0.01 M SnF <sub>4</sub> with 1 : 1, substrate: glass, spin-coating: 1500 rpm for 30 s, annealing temperature: 473–673 K, annealing time: 2–8 h                 | In : Sn atomic ratio = 10 : 1 | ~50                 | 3.85       | ~80% (380–780 nm)           | 993                           | 49                                     | 10        |
| Microwave sintering                          | Precursor solution: 0.2 M (InCl <sub>3</sub> + SnCl <sub>2</sub> ) with atomic ratios of Sn/(Sn + In) = 0–17.0%, substrate: glass, microwave irradiation: 2.45 GHz, microwave power: 700 W                              | 8.0 at% of Sn                 | 900                 | —          | 85% (380–780 nm)            | —                             | 5                                      | 32        |

Table 3 (Contd.)

| Methods   | Experimental conditions  | Optimized doping content | Film thickness (nm) | $E_g$ (eV) | $T_{av}$ (wavelength range) | $R_s$ ( $\Omega$ sq $^{-1}$ ) | $\rho$ ( $\times 10^{-4}$ $\Omega$ cm) | Ref. |
|---|--|--------------------------|---------------------|------------|-----------------------------|-------------------------------|--|------|
| Electron beam evaporation with post-microwave treatment | Electron beam evaporation: raw materials: ITO tablets with $\text{In}_2\text{O}_3$ ; $\text{SnO}_2$ of 90 : 10, substrate: Quartz, deposition time: 1000 s, deposition rate: $1 \text{ \AA s}^{-1}$ , substrate temperature: room temperature - 773 K, post-microwave treatment: frequency: 2.4 GHz, power: 600–1000 W, time: 60 s | 10 wt% of $\text{SnO}_2$ | ~100                | 4.13       | 98.7% (380–780 nm)          | 81                            | —                                      | 6    |
| Inkjet-printing   | Raw materials: ITO nano-particles, ITO content: 15 wt%, disperse: 72 h ball-mill, high speed mixing at 2000 rpm for 8 min, and ultrasonic homogenizing process for 10 min, substrate: quartz   | 10 wt% of $\text{SnO}_2$ |                     | 3.76–3.82  | 87% (380–780 nm)            | 517                           | 300                                    | 33   |

The optimized optoelectronic performance of the ITO thin films fabricated *via* this method is compared with that of films prepared by other reported approaches in the literature, as summarized in Table 3. Evidently, the microwave-assisted spray pyrolysis (MSP) method is well-suited for fabricating ITO films with superior optoelectronic performance. Owing to the merits of rapid and homogeneous heating inherent to microwave irradiation, this heating mode has been integrated into magnetron sputtering,<sup>31</sup> sintering,<sup>32</sup> electron beam evaporation<sup>6</sup> and other thin film deposition techniques, which has further improved the optoelectronic properties of the resultant ITO films. This advantageous effect is also validated in the present work. The ITO films doped with 10 wt%  $\text{SnO}_2$  prepared by MSP exhibit lower electrical resistance and resistivity and higher optical transmittance relative to those fabricated by alternative methods, including traditional spray pyrolysis,<sup>1,4,12</sup> magnetron sputtering,<sup>7,31</sup> atomic layer deposition,<sup>11</sup> sol-gel,<sup>10</sup> and electron beam evaporation,<sup>6</sup> *etc.*

## 4 Conclusions

This study investigates the effects of  $\text{SnO}_2$  doping content (0–20 wt%) on the structural, morphological, optical and electrical properties of ITO thin films prepared by microwave-assisted spray pyrolysis, with the key conclusions summarized as follows:

(1) XRD analysis confirms all films possess a cubic  $\text{In}_2\text{O}_3$  crystal structure under microwave volumetric heating. The undoped  $\text{In}_2\text{O}_3$  film exhibits a (222) preferential orientation, which shifts to (400) upon  $\text{SnO}_2$  doping. Increasing  $\text{SnO}_2$  content enhances film crystallinity and grain size, while reducing the (400) texture coefficient and microstrain of the films.

(2) AFM and cross-sectional SEM characterizations reveal that the surface homogeneity and flatness first increase then decrease with rising  $\text{SnO}_2$  doping content. Film thickness decreases continuously with increasing  $\text{SnO}_2$  content, which is attributed to the combined effects of improved crystallinity and a reduced (400) texture coefficient.

(3) Optical measurements show the average optical transmittance (relative to quartz substrate) rises from 83.56% (0 wt%  $\text{SnO}_2$ ) to 86.12% (15 wt%  $\text{SnO}_2$ ), then decreases to 84.68% at 20 wt%  $\text{SnO}_2$  doping. The obtained band gap  $E_g$  increases remarkably from 3.64 eV (undoped) to 3.85 eV (5 wt%  $\text{SnO}_2$ ), and then fluctuates slightly at  $\sim 3.80$  eV with further doping up to 20 wt%.

(4) Electrical tests demonstrate that  $\text{SnO}_2$  doping significantly enhances the electrical conductivity of ITO films compared to the undoped sample, which originates from the sharp increase in carrier concentration induced by  $\text{Sn}_{\text{In}}$  substitution and oxygen vacancy formation. The sheet resistance  $R_s$  and resistivity  $\rho$  drop drastically from  $288.8 \text{ } \Omega \text{ sq}^{-1}$  and  $170.7 \times 10^{-4} \text{ } \Omega \text{ cm}$  (undoped) to  $7.4 \text{ } \Omega \text{ sq}^{-1}$  and  $1.9 \times 10^{-4} \text{ } \Omega \text{ cm}$  at 10 wt%  $\text{SnO}_2$  doping, while a slight increase in  $R_s$  and  $\rho$  is observed with further doping to 20 wt%.

(5) The figure of merit  $\phi_{\text{TC}}$  confirms that  $\text{SnO}_2$ -doped ITO films have far superior optoelectronic performance to the



undoped In<sub>2</sub>O<sub>3</sub> film. 10 wt% SnO<sub>2</sub> is determined as the optimal doping concentration, yielding films with high optical transmittance and low electrical resistance.

Microwave-assisted spray pyrolysis exhibits excellent adaptability for fabricating high-performance ITO films. The 10 wt% SnO<sub>2</sub>-doped ITO film shows excellent suitability for diverse optoelectronic applications, particularly those requiring high performance transparent conductive electrodes.

## Author contributions

Yulun Feng: writing – review and editing, writing – original draft, formal analysis, data curation; Leyuan Zhang: methodology, formal analysis, writing – review and editing; Haoran Chen: writing – original draft, data curation, formal analysis, resources; Lihua Zhang: visualization, validation, supervision, conceptualization, funding acquisition; Xin Guo: methodology, investigation, formal analysis, conceptualization, resources; Xinya Liu: methodology, investigation, writing – original draft, data curation; Shenghui Guo: project administration, conceptualization, investigation, supervision; Yulun Feng: writing – original draft, resources, data curation, software.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Data will be made available upon a reasonable request to the corresponding authors.

Supplementary information (SI): the relative standard deviation (RSD) of surface roughness, thickness and resistivity of the as-prepared ITO films with different SnO<sub>2</sub> doping content. See DOI: <https://doi.org/10.1039/d5ra09041e>.

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