A novel and potentially scalable CVD-based route towards SnO₂:Mo thin films as transparent conducting oxides

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ABSTRACT

In this report, we prepared transparent and conducting undoped and molybdenum-doped tin oxide (Mo–SnO₂) thin films by aerosol-assisted chemical vapour deposition (AACVD). The relationship between the precursor concentration in the feed and in the resulting films was studied by energy-dispersive X-ray spectroscopy, suggesting that the efficiency of doping is quantitative and that this method could potentially impart exquisite control over dopant levels. All SnO₂ films were in tetragonal structure as confirmed by powder X-ray diffraction measurements. X-ray photoelectron spectroscopy characterisation indicated for the first time that Mo ions were in mixed valence states of Mo(VI) and Mo(V) on the surface. Incorporation of Mo⁶⁺ resulted in the lowest resistivity of $7.3 \times 10^{-3} \Omega \text{cm}$, compared to pure SnO₂ films with resistivities of $4.3(0) \times 10^{-2} \Omega \text{cm}$. Meanwhile, a high transmittance of 83% in the visible light range was also acquired. This work presents a comprehensive investigation into impact of Mo doping on SnO₂ films synthesised by AACVD for the first time and establishes the potential for scalable deposition of SnO₂:Mo thin films in TCO manufacturing.

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GRAPHICAL ABSTRACT

Introduction

Transparent conducting oxides (TCOs) are a type of material based on wide-bandgap metal oxide semiconductors that are simultaneously optically transparent in the visible-NIR light range and electrically conductive as thin films (thickness $< 1\mu\text{m}$). They have been used in a large number of applications, such as flat-panel displays [1], light emitting diodes (LEDs) [2], solar cells [3, 4] and as low-emittance window materials [5]. The most widely used TCO material both in the laboratory and industry is tin-doped indium oxide (ITO), which has a resistivity as low as $1 - 2 \times 10^{-4}\Omega\text{cm}$ and a transmittance over 85% across the visible light range [6]. As electronics industry has been developing rapidly since the 1970s, the demand for ITO, in particular in flat-panel displays, has been increasing significantly [1]. Currently, ITO represents 60% of the transparent conductor market and approximately 60% of indium consumption globally [7]. However, the reserves of indium in the Earth's crust are relatively scarce and it is refractory to purify [8]. Therefore, alternatives to ITO with similar or even better optoelectronic performance must be found.

Semiconductor thin films based on tin oxide (SnO_2) have a large bandgap ($> 3.6\text{ eV}$) that is higher than the visible transparency requirement for TCOs ($> 3.1\text{ eV}$) and possess a resistivity value in the order

of $10^{-2} - 10^{-3}\Omega\text{cm}$ primarily caused by oxygen vacancies [9]. Incorporation of ions with a distinct valence state into host SnO_2 , i.e. aliovalent ion doping, is able to enhance the electrical conductivity via increasing the mobility and carrier concentration [10, 11]. Commonly used doped variants of SnO_2 contain F^- at the anion site which is a good candidate to replace ITO and possesses a resistivity of $\sim 4 \times 10^{-4}\Omega\text{cm}$ and an over 80% transmittance [12–14]. Additionally, antimony (Sb) with a resistivity of around $6 \times 10^{-4}\Omega\text{cm}$ and approximately 80% transmittance [15–17] and tantalum (Ta) [11, 18] at the cation site can also be used as dopants to improve conductivity. Consequently, research on doped SnO_2 is crucial for discovering alternative TCO materials.

To date, a wide variety of synthetic pathways towards doped SnO_2 thin films have been reported including magnetron sputtering, [19] pulsed laser deposition (PLD) [20, 21], spin coating [22–24], spray pyrolysis [15, 25, 26] and aerosol-assisted chemical vapour deposition (AACVD) [11, 12, 27]. AACVD is a variant of conventional CVD which depends on carrier gas transporting precursor aerosols to the deposition zone with elevated temperature. In this modified CVD technique, a precursor or precursors containing the requisite atoms to produce the solid-state materials is dissolved in a solvent and the solution is then placed above a vibrating piezoelectric plate to generate mist. The precursor-infused mist is carried by an inert gas to a reaction chamber containing substrates, heated at the

required temperature for thin-film deposition. Volatility of precursor is not a requirement in AACVD, which considerably expands the choice range of precursors possible. This technique allows precise control over dopant stoichiometry in resultant products as dopant contents in products are directly proportional to the dopant concentration in the precursor solution [28]. Another advantage is that it simplifies the vaporisation and delivery of precursor solution via use of a nebuliser and carrier gas, as compared to conventional CVD, which depends on evaporating volatile precursors to transport precursors to the reaction zone. As a consequence, cost of the deposition process can be lowered [29, 30]. However, good solubility of precursors in certain solvents becomes a vital requirement for this technique, which makes sure the generation of precursor mist. Solvent viscosity should be also considered whilst selecting organic solvents as average small-sized aerosols can be generated more easily from solvents with a lower viscosity; therefore, a successive and homogeneous supply of precursor droplets can be realised and hence improves film growth [31]. Nevertheless, AACVD has several advantages over common thin-film deposition techniques, such as an extensive range of possible precursors that can be utilised owing to the requirement for volatile precursors found in conventional CVD being removed, simple operation, relatively precise control over doping levels due to the bottom-up nature of the process and the potential for scale-up [32]. To be specific, when compared to deposition of thin films by spin coating, which involves a thermal treatment post-deposition for hours, there is no need of such a treatment in AACVD technique, which saves on both processing cost and time.

As a potential candidate of TCOs, research has been directed towards investigation of the effect of Mo on SnO₂ thin films, in particular focusing on the doping impact on optoelectronic performance [33–36]. In this paper, we now report the deposition of SnO₂:Mo thin films via AACVD and the impact of Mo doping on crystal growth mechanics and optoelectronic properties of SnO₂ films prepared were systematically studied by a wide range of characterisation techniques including powder XRD, SEM, Raman spectroscopy and UV–Vis spectroscopy. To the best of the authors' knowledge, synthesis of SnO₂:Mo thin films by AACVD and the effect of Mo doping on the film growth and optoelectronic performance have not been reported yet.

Experimental section

General considerations

The Sn source was butyltin trichloride (C₄H₉SnCl₃, 95%, Sigma-Aldrich), the Mo source was ammonium orthomolybdate ((NH₄)₂MoO₄, 99.98%, Sigma-Aldrich), and the solvent was methanol (99.9%, VWR International, LLC). All chemicals were used as-supplied by manufacturers. Ar (99.99%, BOC, UK) was used as the carrier gas.

Synthesis of SnO₂ thin films by AACVD

Float glass substrates were cut into 1.5 cm × 1.5 cm pieces and were ultrasonically cleansed in aqueous detergent solution, acetone, ethanol and then deionised water for 10 min each step. After cleaning, they were dried in air at room temperature and then put into an ozone cleaner to thoroughly remove organic residues on the surface. The experimental apparatus has been previously described in detail [37, 38]. In a typical experiment, 1.2 mmol of total precursors (i.e. mol (butyltin trichloride) + mol (ammonium orthomolybdate)) was dissolved in 20 mL methanol and the mixture was allowed to magnetically stir for around 15 min to obtain precursor solution with varying molar ratios of butyltin trichloride and ammonium orthomolybdate ($\frac{Mo}{Mo+Sn} = 0, 1, 1.5, 2, 2.5, 3, \text{ and } 5 \text{ mol}\%$), respectively. A flask containing the precursor solution was placed over a piezoelectric nebuliser (the ultrasonic aerosol generator), and hence, aerosols generated were transported to a quartz tube where substrates were horizontally placed. The tube was housed in a tubular furnace. The deposition temperature was 450 °C, the carrier gas flow rate was fixed at 220 cm³/min, and the reaction time was 50 min. After the reaction was complete, the gas flow was not cut out until the furnace temperature dropped below 100 °C. The glass slides were then removed from the tube and stored in the ambient atmosphere for subsequent characterisations.

Characterisation of Mo-doped SnO₂ thin films

Powder X-ray diffraction (pXRD) patterns were obtained using a PANalytical X'Pert MPD X-ray diffractometer utilising Cu radiation ($K\alpha_1 = 1.54056 \text{ \AA}$

and $K\alpha_2 = 1.54443\text{\AA}$) with an intensity ratio of 2:1 at 40 kV and 40 mA. Lattice parameters (a , b and c) and unit cell volumes were calculated by the CELREF software using powder XRD data. Scanning electron microscopy (SEM) images were collected by using a FEI Quanta 250 electron microscope with secondary electron mode at an accelerating voltage of 15 kV. Energy-dispersive X-ray spectroscopy (EDX) was performed in the SEM at an accelerating voltage of 25 kV. Raman spectroscopy was performed on a Renishaw 1000 Raman system with an Ar-laser excitation wavelength of 514 nm, and spectra were acquired over the range of $200\text{--}900\text{ cm}^{-1}$ with a $50\times$ objective at 50% laser power. XPS spectra were measured using a Thermo Scientific Kratos Axis Ultra instrument equipped with a monochromatic Al K_α X-ray source ($h\nu = 1486.6\text{ eV}$). Survey scans were collected in the range $0\text{--}1200\text{ eV}$, and higher-resolution scans were recorded for the main core lines. A charge neutraliser was used to minimise charging and spectra are aligned on the binding energy scale relative to the hydrocarbon C–C/C–H peak at 284.8 eV . Spectra are fitted using Voigt-like peak shapes in the CasaXPS software. Spin-orbit splitting ratios and splitting energies are constrained to obtain physically meaningful fits. The sheet resistance was measured by an Ossila four-point probe station with 25 repeats at room temperature, thereby determining the resistivity ρ combining the thickness values collected by SEM cross-sectional images. Other electrical properties including mobility (μ) and carrier concentration (n) were determined by a home-built Hall effect equipment in the Van der Pauw geometry. A magnetic field of 0.088 T and an input current of 1 mA were applied for the measurement. A Perkin Elmer Lambda 1050 UV–Vis–NIR spectrometer was employed to record transmittance profiles across a wavelength range of $300\text{--}1500\text{ nm}$ against a blank glass reference.

Results and discussion

Compositional analysis of thin films

The elemental compositions of these $\text{SnO}_2\text{:Mo}$ coatings were analysed by energy-dispersive X-ray (EDX) spectroscopy. The observed Mo amount ($\frac{\text{Mo}}{\text{Mo}+\text{Sn}}$ at%) in prepared films is 1.9, 2.1, 2.4, 2.7, 4.4 and 6.9 at%, respectively. The comparison between theoretical

amount and experimentally discovered amount of Mo is displayed in Fig. 1, and the original EDX spectroscopy with calculated component results by atomic percentage is shown in Figure S1 (see Supporting Information). The EDX spectroscopy results confirmed again the successful doping of Mo into SnO_2 films by AACVD. In the plot, an increasing trend and a quasi-linear relationship between theoretical and experimentally found contents of molybdenum are observed, which indicates that control over doping levels within $\text{SnO}_2\text{:Mo}$ films by this technique is possible. To date, such a precise manipulation upon doping levels for $\text{SnO}_2\text{:Mo}$ has not been achieved as far as we are aware.

Structural characterisation of thin films by diffraction

Undoped and Mo-doped SnO_2 thin films were characterised by powder XRD, and the resulting diffraction patterns are displayed in Fig. 2. All thin films analysed present the well-defined single-phase cassiterite SnO_2 with a tetragonal rutile structure, which is in good agreement with the standard card ICDD: 04–008–4169 (rutile, $P4_2/\text{mnm}$).

It is worth noticing that no reflections of any secondary phases are observed in these patterns, which differs from previously reported SnO_2 films synthesised by AACVD, [39] where diffraction peaks belonging to Sn and SnO were observed. Hence, any

Figure 1 EDX spectroscopy of $\text{SnO}_2\text{:Mo}$ thin films: a comparison of theoretical content of doping Mo in the host material and the content found in produced films by EDX. The red dashed line is the linear fitting line ($R^2 = 0.9351$).

Figure 2 PXRD patterns for undoped and Mo-doped SnO₂ thin films deposited via AACVD. Mo atomic percentages are those found experimentally by EDX.

crystalline impurities in our films lie below the limit of detection for pXRD (ca. < 5% w/w). For the undoped thin films, a preferred orientation along the (110) plane is apparent and this preferential crystallite alignment has been reported a number of times previous to this work [14, 40, 41] and is believed to be the most stable crystallographic orientation due to the lowest formation energy [41, 42]. At lower Mo at%, the relative intensities of the other major reflections corresponding to the (101), (200) and (211) planes are increased, suggesting a more random crystallite growth. The (200) plane is thought to be a less closely packed plane; namely, a low atomic density plane and a high intensity of the (200) plane correlate with a high concentration of oxygen vacancies [43]. As we further increase the dopant level, the thin films represent a preferred direction along the (110) plane, as per those doped with 2.7 and

6.9 at% Mo whilst the coatings of 4.4 at% dopant level exhibit a favoured orientation along the (101) plane, which has also been previously reported by Ponja et al. [12], Choi et al. [44] and Kwon et al. [45]. However, no reasonable explanations have been proposed yet. We suggest tentatively that it may be because crystal distortion occurs at high dopant levels, and to maintain crystallographic stability, SnO₂ nuclei will preferentially grow along the plane with a relatively low surface energy. It is generally believed that the (110) plane is of the lowest surface energy, i.e. the most stable crystal plane, and hence, films doped with 2.7 and 6.9 at% Mo grew along with this direction. The (101) plane also has a low surface energy in the rutile SnO₂ structure in line with the first-principles calculations of Oviedo [42]; therefore, the plane (101) in coatings doped with 4.4 at% is the preferred orientation.

The plots of variation in lattice parameters ($a = b, c$) and unit cell volumes against Mo contents in the prepared films are depicted in Fig. 3. An overall declining trend in both lattice parameters and cell volumes is able to be observed, which illustrates that Mo⁶⁺ ions successfully substituted Sn⁴⁺ in the matrix as the Shannon–Prewitt crystal radius of Mo⁶⁺ (60 pm) is smaller than that of Sn⁴⁺ (71 pm) [46]. It is noteworthy that when Mo concentration was at 6.9 at% in the precursor, the volume of the films somewhat increased compared to 4.4 at% films, which was most probably ascribed to the substitution of Mo⁵⁺ (63 pm) [46] (which was detected by XPS and is shown later) as well as Mo⁶⁺ for Sn⁴⁺ in the unit cell as Mo ions at the highest valence state were likely to

Figure 3 Variation in lattice parameters and unit cell volumes of prepared SnO₂ films versus at% Mo found in films.

be reduced to lower states during the deposition procedure [47].

The crystallite size of these coatings was approximated by the Debye–Scherrer equation:

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

where λ is the wavelength of the incident X-rays emitted by the diffractometer, β is the full-width in half-maximum (FWHM) in radians, θ is Bragg diffraction angle and K is the shape factor. Here K was assigned as 0.9 since SnO₂ crystallites in the system could be considered as pseudo-spherical. The planes (110), (101), (200) and (211) were selected to calculate the crystallite size as the intensity of these diffraction peaks is relatively high and the broadened degree is relatively low; therefore, the calculated outcomes are more accurate with less errors. The calculated results (Table 1) displayed that the crystallite size steadily decreased from 40.8 to 32.6 nm with increasing doping Mo dopant level. The decrease is associated with the loss of crystallinity in those films, which is consistent with the XRD analysis presented earlier.

Characterisation of thin films by electron microscopy

Thin-film morphologies

Morphological analysis of the surface of SnO₂ thin films was performed by secondary electron SEM (Fig. 4). Generally speaking, all the coatings consist of homogeneously dispersed and closely packed nanoscale crystallites. For the SnO₂ sample, the crystallites aggregated to form spherical agglomerates with relatively homogeneous size. When the Mo

Figure 4 SEM images of Mo-doped SnO₂ thin films with a variation in dopant levels: **a** 0 at% (SnO₂), **b** 1.9 at%, **c** 2.1 at%, **d** 2.4 at%, **e** 2.7 at%, **f** 4.4 at% and **g** 6.9 at% Mo. The corresponding cross-sectional images are displayed as inset.

dopant concentration increased to 1.9 and 2.1 at%, the films present analogous crystal growth behaviour but have smaller grain size compared to that of undoped films. At 2.4 at% Mo doping, the morphological features transformed from granular particles to slender bar-shaped grains that are intertwined, forming a continuous network. Additionally, it is notable that these rods are covered by a continuous overlayer. This is potentially beneficial to reduce grain boundaries, thereby constructing high-quality transport paths for electrons. Similar morphologies have been reported by Powell et al. [27], Huo et al. [35] and Babar et al. [48] in lightly P-doped, heavily Mo-doped and Sb-doped (medium doping concentration) SnO₂ thin films, respectively. It is plausible that these layers are induced by incorporation of dopants as they have never been observed in pure SnO₂ coatings to date. Nevertheless, the origins of the formation are still unknown and require further investigation. When the doping level is at 4.4 at% Mo and higher, several large aggregated particles appear among smaller grains; in particular, for the films deposited from the precursor of the highest Mo concentration, some grains even approach 1 μ m, suggesting a remarkable crystal agglomerating trend. The agglomerating growth behaviour of crystallites was also discovered in other studies on SnO₂ films [49, 50]. The corresponding cross-sectional images are in the inset of each top-down image, which clearly exhibit the smoothness and uniformity of these thin films. The thickness for each sample was calculated

Table 1 Calculated lattice constants, unit cell volume and crystallite size for the synthesised film

Sample (Mo at% in films)	Lattice constant $a = b/\text{\AA}$	Lattice constant $c/\text{\AA}$	Unit cell volume/ $\text{\AA}^3$	Crystallite size/nm
0	4.7551 (3)	3.1918 (6)	72.161 (4)	40.8 $\pm$ 1.2
1.9	4.7556 (3)	3.1879 (7)	72.097 (2)	34.9 $\pm$ 0.7
2.1	4.7508 (2)	3.1874 (5)	71.966 (4)	31.9 $\pm$ 3.5
2.4	4.7519 (8)	3.1914 (3)	72.083 (1)	33.0 $\pm$ 1.1
2.7	4.7504 (4)	3.1891 (5)	71.975 (1)	32.8 $\pm$ 2.4
4.4	4.7435 (1)	3.1831 (3)	71.622 (5)	33.1 $\pm$ 1.7
6.9	4.7497 (1)	3.1844 (1)	71.838 (6)	32.6 $\pm$ 3.5

using Photoshop software, with an average of 450 nm for all. The large-scale cross-sectional images are depicted in the Supporting Information (see Figure S2).

Dependency of size of aggregates on Mo doping

The evolution of the size of aggregates of all coatings is depicted in Fig. 5. It should be noted those anomalously huge aggregates were not included when calculating the average aggregate size. It can be seen that the average aggregate size presents an overall declining trend (293.9 ± 40.3 nm for pure SnO_2 , 169.6 ± 20.2 nm for 2.4 at% doping level and 103.1 ± 9.7 nm for 6.9 at% doping level), which is likely resulted from lattice distortion and stress induced by the continuously increased doping levels.

Structural analysis of thin films from Raman spectral data

Raman spectra of SnO_2 coatings were measured within the range of $200\text{--}850\text{ cm}^{-1}$ at room temperature (Fig. 6). The Raman peaks centred at 475 , 637 and 775 cm^{-1} in these systems are assigned to Raman active modes for tetragonal rutile SnO_2 : E_g , A_{1g} and B_{2g} , respectively, of which the former is related vibrations in the plane vertical to c -axis whilst the latter two represent vibrations in the plane of the c -axis [51–53]. It is observed that all the aforementioned bands are broadened with decreased intensity in the synthesised films as compared with those of bulk SnO_2 , which has been interpreted previously to

Figure 5 Evolution of the average size of aggregates against Mo doping levels, excluding exceptionally large aggregates.

Figure 6 Room-temperature Raman spectra of prepared SnO_2 thin films against varying at% Mo.

be induced by the nanocrystalline structure of thin films [41, 54]. The A_{1g} band, which appears in all Mo-doped films studied, is shifted to the lower frequency, in particular for 4.4 and 6.9 at% Mo-doped films, compared to the undoped counterpart. This variation is possibly due to reduction in the grain size of these films caused by the Mo incorporation [51], which is consistent with the grain size calculation presented above.

We also note that there is a shoulder-like band next to A_{1g} peak centred at ca. 575 cm^{-1} in all film samples, whereas it is not observed in bulk reference. The appearance of this peak has been attributed to nanoscale SnO_2 and is strongly associated with the atom vibrations in the superficial layers of the nanocrystallites [55, 56]. In addition, the smaller the particle size is, the higher wave numbers the band will shift to and the higher the intensity will be,

which could be confirmed by the contrast between the undoped sample and the samples doped with lower Mo concentration. The peak at 425 cm^{-1} in films doped with high Mo concentration is assigned to an A_{2g} silent phonon mode for bulk polycrystalline SnO_2 . This vibration mode has been reported in SnO_2 nanoribbons [57], but the causes of this mode are not well understood. In low-frequency range, there are three bands with weak intensities centred at 245, 320 and 350 cm^{-1} , which are ascribed to infrared radiation active modes, E_u (TO, the former one) and E_u (LO, the latter two). TO and LO are transverse optical and longitudinal optical, respectively. These bands that are not detected in bulk materials are correlative with the transformation of infrared active modes to Raman active modes resulted from the grain size reduction and particle aggregation [51, 52, 58].

Surface analysis by XPS

XPS was utilised to characterise the valance states and compositional information at the surface of these prepared coatings. The survey scan spectra normalised to the intensity of Sn 3d peaks are displayed in Figure S3 (see Supporting Information). All three representatives have Sn, O, Mo and C at the surface, which is consistent with XRD and EDX analysis. The C element is believed to the residual of organic compounds in the precursor solution. The narrow Mo 3d core-level scan is depicted in Fig. 7. The Mo 3d spectra are fitted with two spin orbit split doublets (again corresponding to $3d_{5/2}$ and $3d_{3/2}$ splitting) with splitting energy of 3.2 eV. All three spectra are dominated by a spin–orbit doublet with peaks at binding energies 232.2 ± 0.1 and 235.5 ± 0.1 eV, which is associated with Mo in the formal (VI) oxidation state. The other spin–split doublet with peaks at 230.9 ± 0.1 and 234.2 ± 0.1 eV are assigned to the valence state of Mo(V) [59]. This demonstrates that part of Mo^{6+} ions was reduced during the film deposition. MoO_2 can be ruled out due to the complex Mo 3d line shape associated with Mo(IV) in MoO_2 [60].

In all cases, the Mo(VI):Mo(V) ratio is roughly 2:1, which is indicative of dominance of Mo(VI) in derived peak of the spectra. It can be reasonably deduced that free carriers in the doped SnO_2 films are generated by mixed types of donors, i.e. Mo^{6+} and Mo^{5+} , which is, to the best knowledge of authors, reported for the first time.

Figure 7 XPS core-level scan spectra of Mo 3d of Mo-doped SnO_2 thin films produced by AACVD. Red dots are the raw data; solid black line is the fitted envelope from the sum of the background (dashed black line) and the individual fitted components (shaded peaks).

The Sn 3d spectra in Figure S3b consist of a spin orbit split doublet with $3d_{5/2}$ and $3d_{3/2}$ peaks at binding energies of 486.3 eV and 494.7 eV, consistent with SnO_2 [61, 62]. O 1s spectra shown in Figure S3c are similar in that they consist of a narrow feature at a binding energy of 530.2 eV which arises from the metal oxide [62]. The broad peak is fitted to account for contamination which will consist of adsorbed hydrocarbons, hydroxides and adsorbed water.

Electrical properties of thin films

The sheet resistance (R_{sh}), electrical resistivity (ρ), and results of the Hall effect measurement including Hall coefficient values, mobility (μ) and carrier concentration (n) are shown in Table 2, and the latter three parameters are plotted in Fig. 8. All SnO_2 thin films doped with Mo behaved as n-type semiconductors, illustrated by the negative Hall coefficient (R_H) values. For pure SnO_2 thin films, the sheet resistance and resistivity are $953.1\ \Omega/\square$ and $4.3(0) \times 10^{-2}\ \Omega\text{cm}$, respectively, which is in general comparable to that of samples synthesised by other techniques [18, 63], including AACVD [11]. For doped SnO_2 thin films, the resistivity was

Table 2 Data of electrical and optical properties of undoped and Mo-doped SnO₂ films

Sample (Mo at%)	<i>d</i> (nm)	<i>R_{sh}</i> (Ω/□)	ρ ($\times 10^{-2} \Omega \text{ cm}$)	Hall coefficient, <i>R_H</i> (cm^3/C)	<i>n</i> ($\times 10^{19} \text{ cm}^{-3}$)	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	<i>T_{400–700}</i> (%)	<i>E_g</i> (eV)	<i>E_u</i> (meV)	Φ ($\times 10^{-3} \Omega^{-1}$)
0	451 ± 9	953.1 ± 43.0	4.30 ± 0.21	− 0.15	4.19 ± 0.52	6.91 ± 0.84	80.70	4.00 ± 0.02	204.3	0.12
1.9	356 ± 8	676.6 ± 8.5	2.41 ± 0.06	− 0.13	4.94 ± 0.33	6.62 ± 0.55	79.69	4.03 ± 0.02	207.7	0.15
2.1	426 ± 7	436.7 ± 6.9	1.86 ± 0.04	− 0.040	15.54 ± 0.26	12.32 ± 1.26	76.39	3.99 ± 0.03	213.6	0.15
2.4	390 ± 15	189.3 ± 20.1	0.73 ± 0.08	− 0.028	22.62 ± 0.67	11.85 ± 0.43	82.77	4.05 ± 0.03	207.4	0.80
2.7	519 ± 19	329.3 ± 33.7	1.71 ± 0.19	− 0.055	11.27 ± 0.46	11.24 ± 0.47	81.60	4.04 ± 0.03	207.0	0.40
4.4	451 ± 8	827.7 ± 11.2	3.73 ± 0.08	− 0.46	1.35 ± 0.13	7.82 ± 0.88	77.29	4.00 ± 0.03	232.8	0.09
6.9	521 ± 19	1390.2 ± 31.2	7.24 ± 0.31	− 0.27	0.23 ± 0.09	3.63 ± 0.38	73.21	3.98 ± 0.01	223.0	0.03

d film thickness; *R_{sh}* sheet resistance; ρ resistivity; μ mobility; *n* carrier concentration; *T_{400–700}* average transmittance in the visible light range; *E_g* optical bandgap; *E_u* Urbach tail; Φ figure of merit

continuously decreased, and the mobility along with carrier concentration simultaneously grew up before the dopant saturation limit was reached. This can be envisaged as substitution of Sn⁴⁺ ions with Mo⁶⁺/Mo⁵⁺ in doped samples, generating free electrons in the conduction band [33, 47]. The presence of Mo⁵⁺ has been confirmed by XPS analysis previously. However, the fact that XPS measurements merely probe a limited thickness of the films (6–10 nm) should be noted. At the doping level of 2.4 at% Mo, the resistivity was substantially reduced to $7.3 \times 10^{-3} \Omega \text{ cm}$, the lowest value in all the systems. Mobility and carrier concentration also gained considerably high values at $11.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.26 \times 10^{20} \text{ cm}^{-3}$, as compared with those of other synthesised samples. These values of electrical properties are comparable to those of doped SnO₂ coatings reported in the literature [41, 63, 64]. Additionally, the continuous layers occurring in the SEM images of 2.4 at% Mo-doped thin films (see Fig. 3d) would reduce to a large extent the grain boundaries and hence improve the electron transport performance within the films. This is another potential reason for achieving the lowest resistivity at 2.4 at% Mo doping level. The resistivity generated from the optimal doping level is comparable and even lower than that of SnO₂:Mo films synthesised by other techniques [35, 65].

Upon increasing the doping amount above 2.4 at%, the conductivity deteriorated, such that an evident growth of resistivity and a declining trend in both mobility and carrier densities were able to be observed. The significant increase in carrier densities would give rise to the falling formation energy of compensating defects such as cation vacancies (*V_{Sn}*), resulting in the reduction in carrier concentration after the dopant limit [66, 67]. In addition, heavy doping suggests increase in the number of ionised impurities in the crystallites, which would lead to the increase in ionised impurity scattering and hence reduce the mobility. When dopant concentration in resulting films was high (4.4–6.9 at%), the SnO₂ aggregates became less continuous and connective, and the aggregate size declined compared to that of samples with lower dopant concentration, which has an adverse impact upon mass electron transport in the host matrix. As a consequence, the mobility experienced a plummet at higher doping contents.

Figure 8 Plot of electrical properties as a function of Mo contents experimentally found in the films.

Optical properties of thin films from absorption spectral data

Absorption spectroscopy was used to investigate the optical properties of the Mo-doped SnO₂ films. Film transmittance profiles in the visible and NIR range (300–1500 nm) are displayed in Fig. 9. The average transmittance of all thin films is approximately 80%, and the highest value is 83% for coatings doped of 2.4 at% Mo content (Table 2), which satisfies the transparency requirement for TCOs (over 80% in the visible range). Interference fringes are observed in the spectrum, which is indicative of the thickness variation consistent with the visible wavelengths of light. The dark colouration can be observed in the films doped with higher Mo amount, in particular for the 6.9 at% sample, and therefore the transparency declined slightly.

The optical bandgap energies for the thin films (E_g) were calculated by the following equation [68]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (2)$$

where α is the absorption coefficient and $h\nu$ is the photon energy, A is the constant and E_g is the optical bandgap. SnO₂ is a direct bandgap semiconductor, and therefore, n should be 2. In the plot of $(\alpha h\nu)^2$ versus $h\nu$ (eV), the estimated bandgap value was generated via extrapolating the linear part at high photon energy to x -axis (see Supporting Information Figure S4). The calculated values are presented in table, and the changing plot is depicted in the inset of Fig. 9. As can be seen, the bandgap is all *ca.* 4 eV and the deviation is only ± 0.05 eV. The Mo doping did

not induce the expansion of bandgap in SnO₂ thin films, i.e. the Moss–Burstein effect (shift of band gap to higher values owing to higher levels of the conduction band being occupied by extra electrons), as usually observed in other doped SnO₂ systems [64, 69]. It is likely due to the limited replacement by Mo⁶⁺ for Sn⁴⁺ in SnO₂ unit cells; therefore, finite higher levels in the conduction band were filled with electrons provided by doping ions. Similar reports of this phenomenon have appeared in the literature where the bandgap energy shift did not appear after the incorporation of Mo ions into matrix SnO₂ films [65].

The appearance of Urbach-type band tails results from the thermal and structural disorder in thin films, and in doped films where structural disorder caused by dopants is predominant [70]. The absorption coefficient empirically follows an exponential dependence on photon energy in the sub-bandgap region, that is [71]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu - E_g}{E_u}\right) \quad (3)$$

where α_0 is the constant, $h\nu$ is the photon energy and E_g is the bandgap. The α follows a dependence on transmittance T [72]:

$$\alpha = -\frac{1}{d} \ln T \quad (4)$$

where d is the film thickness. As a consequence, variation in α versus photon energy can be acquired. The Urbach energy (E_u) describes the width of band tails and can be calculated from the slope of the linear

Figure 9 Variation profiles of transmittance (a) and optical bandgap values (b) for undoped and Mo-doped SnO₂.

fitting line of $\ln \alpha$ versus $h\nu$ (See Supporting Information Figure S5). Larger values demonstrate a greater amount of disorder. The resulting values are recorded in Table 2. An evident increase in Urbach energy values can be observed in films with high doping levels (4.4 and 6.9 at%), compared to those of undoped and doped thin films with lower doping levels, which indicates that an excess quantity of dopants would lead to more lattice disorder.

To compare the performance of different TCOs, the figure of merit (Φ) proposed by Haacke [73] is a useful value to evaluate optoelectronic performance of nascent TCOs:

$$\Phi = T^{10}/R_{sh} \quad (5)$$

where T is the average transmittance in the visible range (400–700 nm) and R_{sh} is the sheet resistance. The calculated results of all coatings are included in Table 2. The highest figure of merit was achieved at films of 2.4 at% dopants. In principle, the higher the figure of merit of a TCO film is, the more superior optoelectronic property it will have. Consequently, the SnO₂ films synthesised from the solution with 2.4 at% Mo possess the greatest performance.

As mentioned above, TCOs with an excellent electronic performance have a high figure of merit. Industrially produced ITO films basically have a figure of merit at the order of $1.2 \times 10^{-2} \Omega^{-1}$. The performance comparison through figure of merit between the present work and reported work in the literature is displayed in Table 3, which suggests that the present performance is comparable to other

produced transparent conducting thin films, and consequently, SnO₂:Mo is a promising complement to ITO although there is other research worth launching, such as finding the optimal tin and molybdenum sources and the corresponding dosage.

Conclusions

In summary, pure and SnO₂:Mo thin films were prepared by AACVD at 450 °C as an alternative to ITO in various applications. Powder XRD patterns of as-grown films showed the films are crystalline and possess the cassiterite SnO₂ tetragonal structure with a preferred growth orientation along the (110) plane relative to the substrate in most films. Top-down SEM images presented a closely packed and uniformly distributed nanocrystals on the surface, and cross-sectional images displayed the smoothness of these films with ~400 nm thickness. EDX results exhibited good agreement between theoretical Mo concentration in the solution and experimentally found amount of Mo in films, indicating an exquisite control over doping levels. Analysis on Raman spectra demonstrated several unique active modes resulting from the nanoscale nature of the coatings in addition to main peaks generally observed in the bulk material. With regard to optoelectronic properties, the optimal doping level (2.4 at% Mo) realised the best performing film with an electrical resistivity of $7.5 \times 10^{-3} \Omega \text{cm}$ and a transmittance of 83% in the visible light range, which is comparable to

Table 3 Comparison of SnO₂:Mo thin films deposited in this work with previously reported doped SnO₂ films deposited by various related techniques

Year	Method	Film	R_{sh} ($\Omega/\square$)	$T_{\lambda 400-700}$ (%)	Φ ($\times 10^{-3} \Omega^{-1}$)	Ref
1990	Reactive evaporation	SnO ₂ :Mo	1200.0	85.0	0.2	[65]
1997	CVD	SnO ₂ :Mo	50.0	80.0	2.2	[33]
2008	Spray pyrolysis	SnO ₂ :Sb	20.2	90.0	17.2	[74]
2011	Spray pyrolysis	SnO ₂ :Nb	70.8	71.5	0.4	[75]
2014	Spray pyrolysis	SnO ₂ :Mo	81.6	81.1	1.5	[34]
2017	Mist CVD	SnO ₂ :W	360.0	70.0	0.08	[35]
		SnO ₂ :Mo	960.0	61.0	0.007	
2018	AACVD	SnO ₂ :Sb	9.0	62.5	1.0	[12]
2019	Spray pyrolysis	SnO ₂ :Sb	31.9	77.5	2.4	[15]
2020	AACVD	SnO ₂ :Ta	8.0	64.1	1.4	[11]
This work	AACVD	SnO ₂ :Mo	189.3	82.8	0.8	–

transparent conductive films prepared in the literature in accordance with the figure of merit comparison. The results illustrate that SnO₂:Mo thin films synthesised by AACVD are potential candidate TCOs even though other studies need to be developed to complete systematic investigations.

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Declaration

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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