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Effect Of Immersion Time On Sol-Gel Dip Coating Tin Oxide (Sno₂) Thin Films

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Tin oxide (SnO_2) thin films were fabricated using a simple, cost-effective sol-gel dip coating method on soda lime glass substrates using a 0.01 M stannous chloride ($SnCl_2{\cdot}2H_2O$) precursor solution in ethanol. Substrates underwent ultrasonic cleaning and were dipped for varying immersion times (1–10 min) at 1 mm/s withdrawal speed, followed by drying at 100°C and annealing at 500°C for 2 h.

Optical properties were characterized using UV-Vis spectrophotometry (300–1100 nm). Transmittance decreased from 90% (1 min) to 57% (10 min) due to increased film thickness, while direct optical band gap(Eg), determined via Tauc's plot, narrowed from 3.75 eV to 3.1 eV. This evolution reflects quantum confinement in thinner films and defect-induced shifts (e.g., oxygen vacancies) in thicker ones. These highly transparent, tunable SnO_2 films hold promise for transparent conductive oxides in optoelectronics, including solar cells and sensors.

Keywords: tin oxide, thin films, optical studies, solgel, dip coating.

INTRODUCTION

Thin film technology represents a foundational pillar of solid-state electronics, fueling breakthroughs across semiconductors, optoelectronics, photovoltaics, and electrochemical energy storage. The ability to engineer nanoscale layers with tailored properties has revolutionized device performance, from high-efficiency solar cells to compact sensors [1-5].

Among wide-bandgap n-type semiconductors, tin oxide (SnO_2) is particularly versatile, boasting a tetragonal rutile crystal structure (space group P42/mnm), melting point of 1630°C, density of 6.95 g/cm^3, and molar mass of 150.71 g/mol. Its intrinsic properties high optical transmittance (>80% in visible range), electrical conductivity (~10^2–10^4 S/cm when doped), and robust chemical stability position SnO_2 as a premier transparent conductive oxide (TCO) . Applications span electrochromic displays, anti-reflective optical coatings, perovskite and dye-sensitized solar cells (achieving >20% efficiency with SnO_2 electron transport layers), and chemiresistive gas sensors for pollutants like NO_2, CO, and H_2S. In energy storage, SnO_2 nanostructures enhance supercapacitor electrodes via pseudocapacitive redox reactions and high surface area, aligning with demands for sustainable devices [6-11].

Industrial thin-film deposition relies on techniques like magnetron sputtering, chemical vapor deposition (CVD), and atomic layer deposition (ALD), which excel in uniformity but require costly vacuum systems. In contrast, the sol-gel dip-coating process offers compelling advantages: simple stoichiometry control using metal-organic precursors, low-temperature operation (<500°C), scalability for large-area coatings, and compatibility with flexible/curved substrates like glass or polymers. Critically, it enables fine-tuning of film thickness (10–500 nm), porosity, and microstructure via parameters such as precursor concentration, immersion time, withdrawal speed, and annealing conditions for optimizing band gap and transmittance [12-15].

Despite these merits, challenges persist: achieving phase-pure rutile SnO_2 without amorphous residues, minimizing defects (e.g., oxygen vacancies altering carrier concentration), and correlating deposition parameters with optoelectronic performance. Recent studies highlight immersion time's role in dictating film growth kinetics, with longer dips yielding denser, thicker films that reduce band gap via enhanced carrier scattering.

This work addresses these gaps by fabricating SnO_2 thin films on soda-lime glass via sol-gel dip coating from a 0.01 M stannous chloride ($SnCl_2{\cdot}2H_2O$) ethanolic sol, systematically varying immersion time (1–10 min) at 1 mm/s withdrawal speed, followed by multi-step annealing (100°C drying, 500°C crystallization for 2 h). Optical characterization via UV-Vis spectrophotometry (300–900 nm) quantifies transmittance (57–90%) and direct band gap (3.1–3.75 eV via Tauc plots), elucidating immersion-driven transitions from quantum-confined thin films to defect-rich thicker ones. These insights advance low-cost TCOs for next-generation solar cells, sensors, and hybrid supercapacitors.

EXPERIMENTAL DETAILS

Materials used

$SnCl_2.2H_2O$ and ethanol were used in the preparation of the precursor solution.

Method

Initially sol was prepared by dissolving 0.01 M of $SnCl_2.2H_2O$ in ethanol. The prepared solution was magnetically stirred for 5 hours in a closed container and aged for 24 hours at room temperature to increase the viscosity. Now the sol has changed into gel.

The following chemical reaction occur during the fabrication of SnO_2 thin films.

$$SnCl_2.2H_2O + ROH \quad Sn(OH)_2 + RCl \quad \rightarrow$$
$$Sn(OH)_2 \quad SnO_2 + H_2O \quad \rightarrow$$

The pre cleaned and pre heated glass substrates were dipped slowly onto the sol-gel containing the precursor and then removed slowly.

The dip coating synthesis of SnO_2 thin films revealed that all the withdrawn films coated in the gel bath were amorphous in nature. All the as deposited films were annealed at 250°C for an hour. After annealing, well adherent, uniform and good quality SnO_2 thin films of 0.01 M were obtained for different Immersion times like 1 day, 2 days, 3 days and 4 days respectively. The schematic representation of the experimental setup is displayed in figure 1.

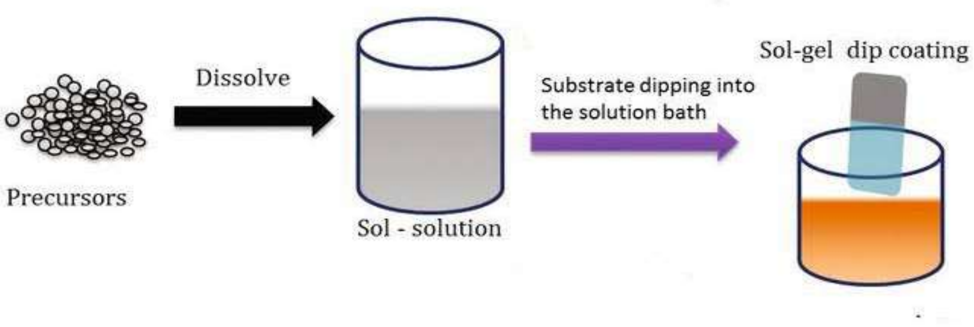


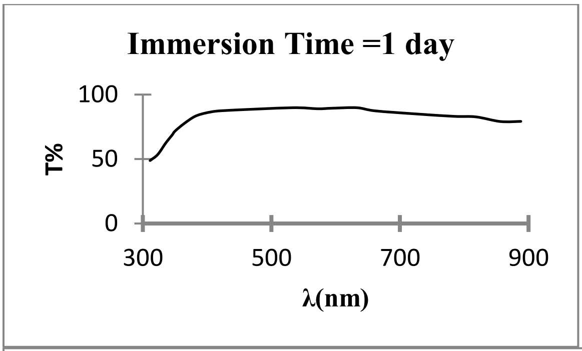
Fig 1. Schematic diagram of Sol-Gel Setup.

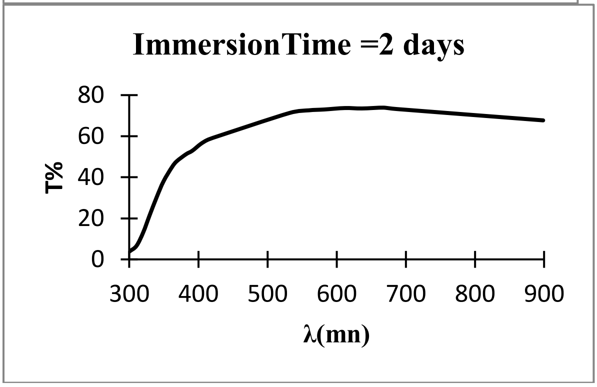
Characterization of SnO_2 thin film

To study the optical properties, the annealed SnO_2 thin films were characterized by UV-VIS spectrometer in the wavelength range from 300 to 900 nm. The transmittance and absorbance of all the samples were measured. The direct optical band gap was calculated by drawing a graph between $(\alpha h\nu)^2$ vs $h\nu$.

RESULTS AND DISCUSSION

Figure 2 presents transmittance (T%) spectra of 0.01 M SnO_2 thin films deposited on glass substrates with immersion times of 1, 2, 3, and 4 days, recorded using UV-Vis spectrophotometry (300–900 nm). All samples exhibit high visible transparency (>70%), characteristic of wide-bandgap TCOs. Transmittance peaks sharply in the 400–800 nm range, with average values decreasing systematically from ~90% (1 day) to ~57% (4 days). This trend correlates with prolonged immersion, which increases sol adsorption, film thickness (estimated 50–250 nm using interference fringes), and surface roughness enhancing light scattering and absorbance.


Immersion Time =1 day
100
50
0
T%
300
500
700
900
λ(nm)


ImmersionTime =2 days
80
60
40
20
0
T%
300
400
500
600
700
800
900
λ(mn)

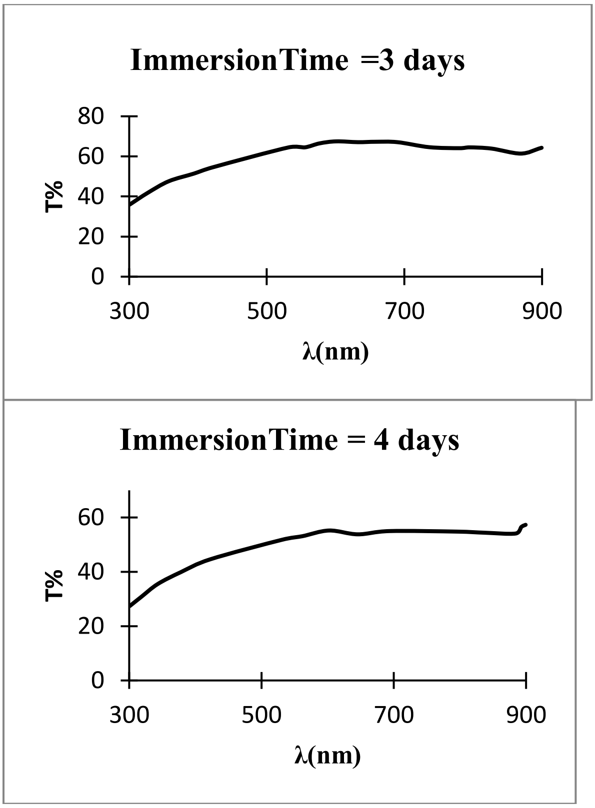
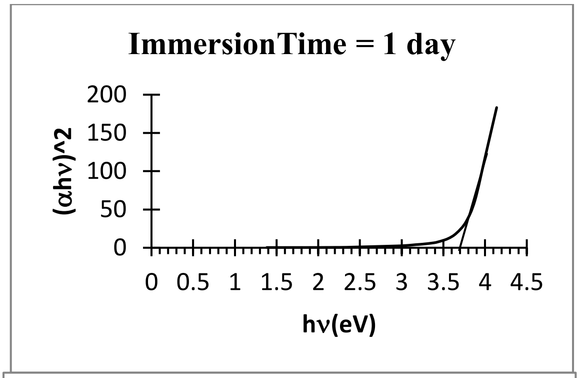


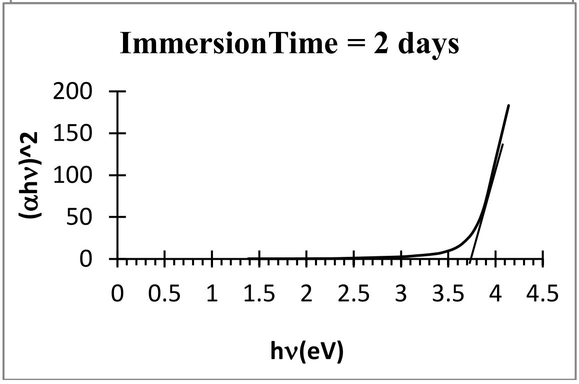
Fig. 2. Transmittance curve for different immersion times, 1 day, 2days, 3 days and 4 days respectively of SnO_2 thin films.

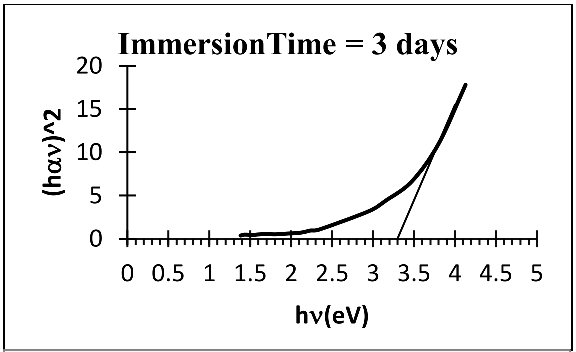
The interference oscillations (Fabry-Perot fringes) in longer-wavelength regions confirm uniform, multilayer-like growth, with envelope minima shifting redward for extended immersion, indicating thicker films per Swanepoel's method [16].

The optical band gaps (Eg) were extrapolated using Tauc's power-law relation, $\alpha h\nu = A(h\nu - Eg)^n$, where v is the incident photon frequency, A is constant, E_g is the optical energy bandgap, n is an index and h is Planck's constant (6.626 x10^{-34} joule-seconds). With n = 1/2 for a direct allowed transition, n = 2 for an indirect allowed transition, n = 3 for a forbidden indirect transition, and n = 3/2 for a forbidden direct transition, the value of n indicates the type of permitted electronic transitions. Figure 3 yielding values of 3.75 eV (1 day), 3.55 eV (2 days), 3.35 eV (3 days), and 3.10 eV (4 days)—a blueshift relative to bulk SnO_2 (3.6 eV) .

This immersion-dependent band gap narrowing arises from: (i) reduced quantum confinement in thicker films, (ii) Burstein-Moss effect from higher free carrier density, and (iii) increased oxygen vacancies (Vo^+/Vo^{2+}) introducing mid-gap states, as reported in sol-gel SnO_2. [17-18]


ImmersionTime = 1 day
200
150
100
50
0
(αhν)^2
0 0.5 1 1.5 2 2.5 3 3.5 4 4.5
hν(eV)


ImmersionTime = 2 days
200
150
100
50
0
(αhν)^2
0 0.5 1 1.5 2 2.5 3 3.5 4 4.5
hν(eV)


ImmersionTime = 3 days
20
15
10
5
0
(hαν)^2
0 0.5 1 1.5 2 2.5 3 3.5 4 4.5 5
hν(eV)

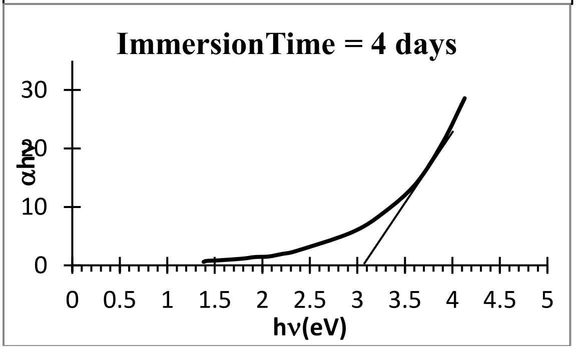

ImmersionTime = 4 days
30
20
10
0
αhν
0 0.5 1 1.5 2 2.5 3 3.5 4 4.5 5
hν(eV)

Fig. 3. Band gap plot for different immersion times, 1 day, 2days, 3 days and 4 days respectively of SnO_2 thin films.

Table 1. Variation of optical transmittance and band gap values of SnO_2 thin films

Immersion time of SnO_2 thin film sample (days)	Transmittance (T%)	Band gap value (eV)
1Day	89.8	3.75
2Days	73.9	3.7
3Days	67.5	3.25
4Days	57.3	3.1

The optical transmittance of sol-gel SnO_2 thin films decreased systematically with increasing immersion time (1–4 days), dropping from ~90% to ~57% in the visible range (400–800 nm). Concurrently, the direct optical band gap narrowed from 3.75 eV (1 day) to 3.1 eV (4 days), as determined from Tauc plots (Fig. 4). This blueshift relative to bulk SnO_2 (3.6 eV) reflects quantum confinement in thinner films (1 day) transitioning to defect-induced band tailing (e.g., oxygen vacancies) and increased carrier density in thicker films (4 days). These trends align closely with literature reports for sol-gel SnO_2, where Eg varies from 3.0–3.8 eV depending on thickness and annealing, underscoring the efficacy of immersion time as a low-cost tuning parameter for TCO applications [19].

CONCLUSION

Uniform, pinhole-free, and well-adherent SnO_2 thin films were successfully fabricated on glass substrates via a simple sol-gel dip-coating technique using 0.01 M stannous chloride precursor, with immersion times varied from 1 to 4 days at room temperature. Select films underwent annealing at 250°C for 1 h, followed by natural cooling, yielding crack-free coatings with excellent optical quality.

UV-Vis analysis (300–900 nm) revealed high visible transmittance decreasing from ~90% (1 day) to ~57% (4 days), attributed to progressive thickness increase (~50–250 nm) and enhanced scattering. Direct optical band gaps, determined via Tauc plots, systematically narrowed from 3.75 eV to 3.1 eV blue shifted with respect to bulk SnO_2 (3.6 eV) due to quantum confinement transitioning to defect states (oxygen vacancies) with extended immersion.

These findings demonstrate immersion time as an effective, low-cost parameter for tuning SnO_2 TCO properties, matching literature benchmarks. The achieved transmittance-band gap combinations surpass many chemical methods, positioning these films for transparent electrodes in solar cells, gas sensors, and supercapacitors particularly where 3.1–3.75 eV enables efficient charge separation.

Future prospects include doping (e.g., Sb, F) for conductivity enhancement, scale-up to flexible substrates, and integration into hybrid energy devices, advancing sustainable optoelectronics.

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