



DEPOSITION AND CHARACTERISATION OF TIN (IV) OXIDE (SnO₂) MODIFIED WITH LIGNIN

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<https://dx.doi.org/10.4314/coast.v7i2.29s>

Abstract

Tin dioxide (SnO₂) thin films modified with lignin was successfully deposited using spray pyrolysis techniques. Lignin, a natural and abundant biopolymer, was incorporated as a functional additive to improve the structural and optical properties of the SnO₂ films. The films were deposited on a glass substrate annealed to study the influence of thermal treatment on film structure and crystallinity. Tetragonal rutile SnO₂ was clearly detected by XRD and slight changes in the peak positions showed that both lignin and SnO₂ had interacted. The use of UV-Vis spectroscopy indicated an adjustable optical band gap where the band gap reduced from 3.72 eV to 3.63 eV as the percentage of lignin increases that suggests greater absorption of visible light due to the addition of lignin showing that lignin changes the electron features of SnO₂, making the films useful for UV protection. Incorporating lignin resulted in better UV absorption, causing a decrease in UV transmittance, yet the samples remained transparent in the visible wavelengths. The modified films exhibited improved surface wettability and potential for enhanced charge transport, making them promising candidates for applications in sensors, photocatalysis, and optoelectronic devices. This work demonstrates a sustainable approach to tailoring metal oxide thin films using renewable biomass-derived materials.

Keywords: Tin (IV) oxide (SnO₂); Lignin; Deposition; Characterisation; Optical Properties.

Introduction

Tin dioxide (SnO₂) thin films have garnered significant attention in the realm of materials science and engineering due to their versatile properties suitable for various technological applications (Johnson *et al.*, 2019; Mai *et al.*, 2019; Nwanna *et al.*, 2020). Tin (IV) Oxide (SnO₂) is a widely utilized wide

bandgap semiconductor with a bandgap of approximately 3.6 eV. Its significant properties, including high electrical conductivity, optical transparency, and chemical stability, render it ideal for various applications. SnO₂ thin films are particularly valuable in technologies that demand both high transparency in the visible spectrum and

excellent electrical conductivity. These films are critical in applications such as transparent conductive coatings for displays and touchscreens, gas sensors for environmental monitoring, and photovoltaic devices for solar energy (Rahal *et al.*, 2015). SnO₂ is a wide-bandgap semiconductor with transparency in the visible range, high stability under different environmental conditions, and excellent electrical conductivity when doped or modified appropriately (Bissig *et al.*, 2015; Sayeed & Rouf, 2021). These characteristics make SnO₂ particularly attractive for applications such as gas sensors (Wang & Haick, 2013), transparent electrodes (Johnson *et al.*, 2019), solar cells (Leyden *et al.*, 2014), and photocatalysis (Nwana *et al.*, 2020).

Tin(IV) oxide (SnO₂) films have been deposited using various techniques, including pulsed laser deposition (PLD) (Kim *et al.*, 2012), Sol-gel method (Jeng, 2012), atomic layer deposition (ALD), and chemical vapor deposition (CVD) (Feng *et al.*, 2008). The unique properties of SnO₂ have led to extensive research on modifying its properties to enhance its performance in various applications. One technique that works well for producing thin films is spray pyrolysis because it is simple to add different doping materials, requires little setup costs, is repeatable, expands rapidly, and can yield large areas of uniform coatings in large quantities—which are crucial for solar cell and industrial applications (Ajanaku & Olutimehin, 2025). As a result, doping SnO₂ thin films to produce multifunctionality has been a widespread practice among researchers, various elements like Al (Bhat *et al.*, 2007; Ravichandran & Thirumurugan, 2014), In (Benouis *et al.*, 2011; Lekshmy & Joy, 2014), Sb (Li *et al.*, 2010) and Zn (Ravichandran *et al.*, 2013) have been used

to dope SnO₂ to address the shortcomings of semiconductors oxide wide energy band gap and high resistive capacity. (Oluyamo *et al.*, 2022). One approach is the incorporation of lignin, a complex organic polymer derived from plant cell walls, which has shown promising results in modifying the properties of SnO₂ thin films. Lignin is known for its biodegradability, renewability, and ability to act as a natural antioxidant (Adebayo & Ajanaku, 2025). Its complex molecular structure, composed of various phenylpropane units linked together through different types of bonds, gives lignin unique chemical and physical properties, including UV absorption capabilities antioxidant behavior and potential electron donor characteristics (Adebayo & Ajanaku, 2025). This work aims to improve the characteristics of SnO₂ thin films by modifying them with lignin, a naturally occurring polymer obtained from biomass. The primary difficulty is figuring out how the addition of lignin modifies the structural, chemical, optical, and electrical properties of SnO₂ and how to best utilize these changes for real-world applications. This study intends to close the information gap about the viability and possible benefits of using lignin as a sustainable and efficient modifier for SnO₂ thin films by examining the deposition techniques and carefully analyzing the resultant composite materials.

Methodology

Preparation of Precursor Solution

Dissolution of Tin (IV) Salt: Tin (IV) chloride, a source of SnO₂ ions, is dissolved in distilled water. Hydrochloric acid (HCl) is added dropwise to stabilize the solution and prevent the hydrolysis of tin ions, which could lead to the premature formation of SnO₂ particles. The solution is stirred at room temperature for about 30 minutes to ensure complete dissolution and homogeneity. It is then

filtered to remove any particulates that could disrupt the smooth deposition of the thin film. The SnO₂ solution is stored in a clean environment, until it is required for use.

Extraction of Lignin: Lignin is extracted from palm kernel shells using an alkaline solution of NaOH. The biomass is first ground into a fine powder, then treated with the NaOH solution at elevated temperatures, typically around 80-100°C, to break down the lignocellulosic structure and release lignin. The lignin solution is then neutralized with H₂SO₄ to precipitate lignin out of the solution. The precipitated lignin is collected by filtration and washed with distilled water to remove any residual acid. The lignin is further purified by washing with ethanol, which helps remove any remaining impurities and enhances the solubility of lignin in the final composite solution.

Solution Preparation: The purified lignin is dissolved in ethanol to prepare the precursor solution. This solution is then stirred continuously until a homogenous mixture is achieved.

Doping of the thin film: The dopants are introduced into the precursor solutions at controlled concentrations. The dope SnO₂ solutions are prepared separately, ensuring that the dopant atoms are evenly distributed throughout the solution, the SnO₂ solutions were mixed with the prepared lignin solution. The mixture is stirred continuously to ensure a uniform distribution of all components, creating a homogenous precursor solution ready for deposition.

Deposition of Thin Films: After obtaining a transparent blend of appropriately diluted Tin (IV) chloride, the prepared lignin solution was introduced into the precursor solution by volume, varying in increments of 1%, 2% and 3%. The substrates used for

this study was a microscopic glass slide with an average weight of 4.850g, a thin flat piece of glass, typically 75 by 26mm (3 by 1) and about 1mm thick. After the substrates is cleaned with liquid soap and water, it was dried, and then submerged in ethanol to remove any remaining water particles. Finally, they were submerged in acetone before being prepared for the thin film deposition process using spray pyrolysis techniques. The deposition was performed in a fume cupboard so as to expelled all the harmful gases that might be present during the deposition process. The precursor solution was transferred as an aerosol onto the substrate using compressed air which served as a carrier gas. The temperature at which the deposition was done was 100°C. It took about 35 minutes to finish the deposition process for one sample. The precursor solution was sprayed at a rate of 0.037 mls⁻¹. The substrates and the spray gun nozzle were spaced 50 centimeters apart. Samples were deposited while maintaining a constant substrate temperature between 100 °C. This drying process can be accelerated by placing the substrates in a low-temperature oven or by air drying in a controlled environment. Annealing is a critical step in the thin film preparation process, as it enhances the structural integrity and crystallinity of the films deposited. This process involves heating the thin films to a specific temperature, promoting the growth of crystalline phases within the composite material.

Results and Discussion

Optical properties

Absorbance of the deposited thin films

The films undergo optical characterization using UV-Vis spectroscopy which involves measuring the absorbance and transmittance of the deposited thin film as a function of wavelength. The transmittance and absorbance spectra of deposited SnO₂ thin films and SnO₂ modified with lignin were

recorded in the wavelength range of 200–800 nm as shown in Figure 1 and Figure 2. This range covers the ultraviolet (UV) region (200-400 nm) and the visible light region (400 - 800 nm), which are important for determining the material's transparency and band gap energy. The graph of absorbance against wavelength is shown in Figure 1 both deposited SnO₂ thin films and the deposited SnO₂ modified with lignin are shown in the graph. The results highlight the absorbance behavior of pure SnO₂ and SnO₂ modified with lignin. For pure SnO₂, strong absorption occurs in the UV region, specifically between 200 nm and 300 nm, with a sharp peak observed around 250 nm. Beyond this point, the absorbance gradually decreases across the visible

spectrum, indicating a reduction in light absorption as the wavelength increases. It was noticed that all SnO₂ thin films modified with lignin has highest absorbance between 250 nm to 300 nm which indicate that the lignin has strong absorbance at the UV region. The incorporation of lignin led to a noticeable shift in the absorption edge, which is indicative of changes in the electronic structure of the SnO₂ thin film. This shift suggests that lignin, acting as a dopant, alters the energy states in the material, possibly by introducing localized states within the band gap or by affecting the crystallinity and defect structure of the SnO₂ matrix according to (Sayeed & Rouf, 2021; Patil & Chavan, 2022; Mezyen *et al.*, 2023).

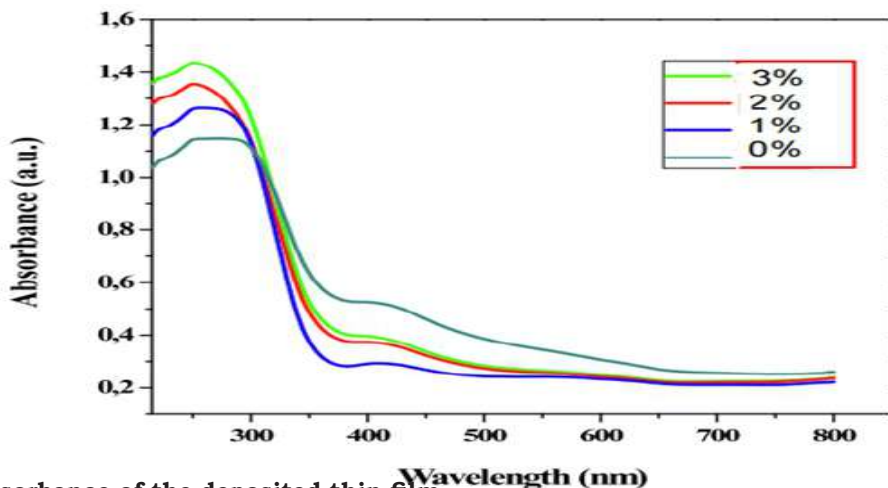


Figure 1 Absorbance of the deposited thin film

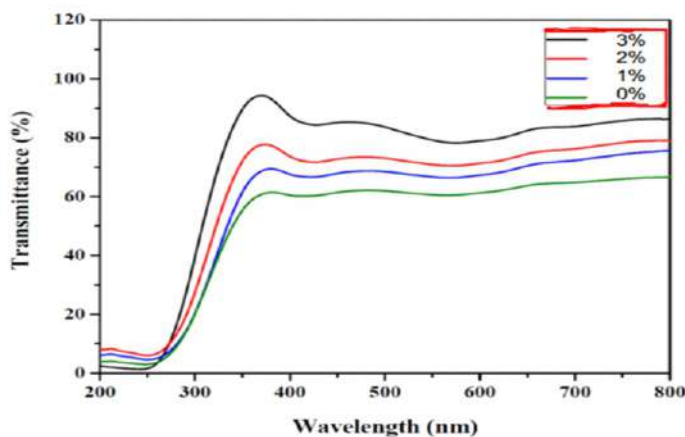


Figure 2 Transmittance of the deposited thin film

Figure 2 indicates the transmittance against wavelength shown in for both deposited SnO₂ thin films and the deposited SnO₂ modified with lignin are shown in the graph. The results highlight the transmittance of pure SnO₂ and SnO₂ modified with lignin. For pure SnO₂, has the second to the lowest transmittance in the UV region, specifically between 200 nm and 250 nm, with a sharp increase in transmittance of 250 nm for all the deposited thin film was observed with SnO₂ thin film modified with 3% lignin has the highest transmittance from 300 nm and 800 nm. The average percentage transmittance is within the range of 70% to 82%. These observed values of maximum transmittance are similar to the value reported by Martinez-Gazoni, *et al.*, (2018), and are within the acceptable transmittance values suitable for application as Transparent Conducting Oxide in optoelectronic devices like solar cells (Cisneros-Contreras *et al.*, 2023). This indicates a degree of transparency, though not perfect, and suggests the film is likely being used in applications where some light transmission is desired but not necessarily all of it. It can be used as optical filters were allowing a specific range of wavelengths to pass through while blocking others. Also, solar cells in which some transparent conductive oxides (TCOs) in solar cells have transmittance values around 70-80%. They allow a good amount of sunlight to reach the active layer while also providing electrical conductivity.

Energy Band Gap of the Deposited Thin Film

The optical band gap of both doped and undoped SnO₂ thin films was calculated by extrapolating the linear portion of the Tauc plot. The Tauc plot is a graphical method used to determine the band gap energy, where $(\alpha h\nu)$ is plotted on the vertical axis, and $h\nu$ (photon energy) is plotted on the horizontal axis. A progressive decrease in the optical energy band gap of SnO₂ thin films was observed with increasing lignin incorporation. This behavior is attributed to the introduction of localized states within the band structure of SnO₂ by lignin's aromatic and functional groups, which effectively narrow the band gap. The result suggests an enhanced absorption in the visible region and a tunable electronic structure, potentially improving the films' performance in optoelectronic and photocatalytic applications. The reduction indicates that the doping with lignin influences the electronic structure of the material, making it absorb light at lower energies. However, the change in the band gap is not drastic, suggesting that the doping primarily affects the UV absorption properties rather than significantly altering the semiconductor behavior of the thin film. It was shown Table 1, the pure SnO₂ thin film has a slightly larger band gap compared to the those modified with lignin samples. This confirms that the incorporation of lignin reduces the band gap, enhancing the material's ability to absorb UV light.

Table 1: Energy Gap of deposited SnO₂ thin film

S/N	Percentage of Lignin	Energy Band Gap
1	0%	3.72eV
2	1%	3.68eV
3	2%	3.66eV
4	3%	3.63eV

Structural properties

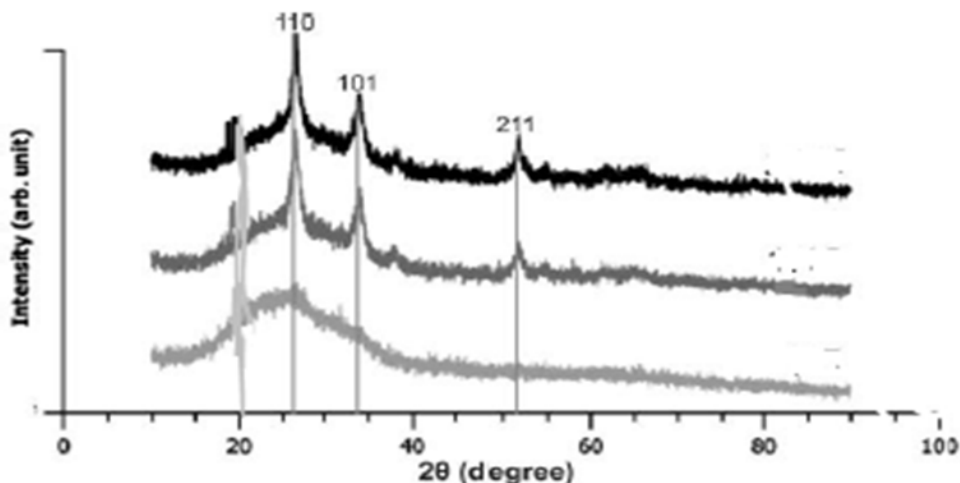


Figure 3: XRD pattern of the deposited thin film

Fig. 3 shows the XRD pattern of the deposited SnO₂ thin films and SnO₂ modified with lignin thin films. It was noticed that the peaks correspond to the orthorhombic structure of SnO₂ thin films (JCPDS card no.04-015-3276) (Barakat *et al.*, 2018). It was observed that the crystallite size and the d-spacing of the fabricated thin films decreased with increasing annealing temperature (Sayeed and Rouf, 2021). The films are typically polycrystalline in nature, with preferred orientations along specific planes. The dominant orientations were observed along the (211), (101) and (110) planes which correlate with Babar *et al.*, 2011; Mezyen *et al.*, 2023.

Conclusion

In summary, we have presented a study describing the change in structural, and optical properties of Tin (IV) oxide thin films modified with lignin which is a biopolymer deposited on a glass substrate using spray pyrolysis. The optical properties of the SnO₂ thin film and the SnO₂ modified with lignin indicate incorporation of lignin led to a noticeable shift in the absorption edge, which is indicative of changes in the

electronic structure of the SnO₂ thin film. SnO₂ thin film exhibited a typical transmittance profile with a sharp absorption edge in the UV region, indicating its high transparency in the visible range. This is consistent with the known properties of SnO₂ as a transparent conducting oxide, which combines good electrical conductivity with high optical transparency. The optical transmittance of the deposited tin film in the visible region with an average transmittance of 72–80% being obtained. It was observed that there is a slight reduction in the energy band gap as lignin is incorporated into the SnO₂ films. The reduction indicates that the doping with lignin influences the electronic structure of the material, making it absorb light at lower energies. The structural properties indicates that the deposited thin films are typically polycrystalline in nature, with preferred orientations along specific planes. The dominant orientations were observed along the (211), (101) and (110) planes which correlate with other researchers. The deposited thin films indicate

a degree of transparency, though not perfect, and suggests the film is likely being used in applications where some light transmission is desired but not necessarily all of it. It can be used as optical filters were allowing a specific range of wavelengths to pass through while blocking others. Also, solar cells in which some transparent conductive oxides (TCOs) in solar cells have transmittance values around 70-80%.

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