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Investigation of Surface Morphology and Electrical Properties of Ti-Doped ZnO Thin Films Using Digitally Controlled Chemical Spray Pyrolysis Technique

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ABSTRACT
This study presents an investigation of the morphology and electrical properties of ZnO as well as Ti-doped ZnO thin films, utilizing a fabricated digital spray pyrolysis device at 350°C. It aims to evaluate the influence of titanium (Ti) doping on the morphology and electrical properties of ZnO thin films in order to assess their suitability for solar photovoltaic applications. Thin films of both ZnO and Ti-ZnO were prepared from extremely pure zinc acetate ($Zn(CH_3COO)_2.2H_2O$) as well as titanium dioxide (TiO_2) precursors. According to scanning electron microscope micrographs, the findings of both the undoped and doped films were seen to be evenly distributed across the substrates. The energy dispersive X-ray results indicated that Zn, O, and Ti were present in the films' elemental composition. The films I-V characteristics demonstrated an improvement of current as the doping increases, with 6% Ti-doped ZnO having the highest conductivity at $7.52 \times 10^2\ S/m$. Thin films of ZnO doped with Ti produced in this investigation have morphological and I-V properties that suggests possible applicability in photovoltaic systems.

Keywords:
ZnO,
Digital controlled spray pyrolysis technique,
Morphology,
Solar cells,
Thin films.

INTRODUCTION

Today, it is a major challenge for humanity to provide clean and sustainable energy. Solar energy is most reliable among several energy sources available because it is fueled by sun and the sun releases a huge quantity of energy at no cost (Babatunde and Odunaike, 2023). To this end, it needs to be underlined that solar energy is the cleanest and most unlimited of all renewable and sustainable energy sources (Bancheva-Koleva *et al.,* 2025). Photovoltaic (PV) devices, which convert sunlight directly into electricity, have gained significant attention for applications ranging from small-scale domestic systems to large-scale power generation. However, the widespread adoption of conventional silicon-based solar cells is limited by their high production cost, motivating the search for low-cost and efficient alternatives (Owoeye *et al.,* 2023).

Thin-film solar cells have emerged as viable candidates due to their reduced material consumption, ease of fabrication, and tunable properties. Among these, zinc oxide (ZnO) is widely used as a transparent conducting oxide and photoelectrode material because of its wide band gap, high exciton binding energy, chemical stability, and low cost (Hussaini *et al.,* 2026; Olumurewa *et al.,* 2022). Despite these advantages, the performance of ZnO is often limited by high carrier recombination and relatively low electrical conductivity, which restrict its efficiency in photovoltaic applications.

To overcome these limitations, doping ZnO with suitable elements has been extensively explored as an effective strategy to tailor its electrical and structural properties. Transition metal dopants such as Ti, Sn, and Mg have been shown to modify carrier concentration, grain structure, and optical behavior (Nurfania *et al.,* 2025). In particular, titanium (Ti) doping is attractive because Ti^{4+} ions can substitute Zn^{2+} in the lattice, introducing additional free electrons and thereby enhancing electrical conductivity (Orelusi *et al.,* 2023). However, the extent of improvement depends strongly on dopant concentration and synthesis conditions.

Previous studies have demonstrated that Ti doping improves ZnO thin films, but the reported outcomes vary depending on the fabrication method. For instance, Rajasekaran *et al*. (2020) reported increased surface roughness and improved optical transparency in Ti-doped ZnO films prepared via spray pyrolysis, while Sridhar *et al.* (2013) observed a significant reduction in resistivity with increasing Ti concentration. Similarly, Devanarayanan *et al.* (2025) showed that dopant incorporation influences crystallinity and band gap tunability. Although these studies confirm the importance of dopant engineering, they also reveal inconsistencies in morphology, electrical behavior, and optimal doping levels, largely due to differences in deposition techniques and process control.

Spray pyrolysis remains a widely used deposition method due to its simplicity, low cost, and suitability for large-area coatings. However, conventional spray pyrolysis systems often suffer from poor control over deposition parameters such as precursor flow rate, droplet size, and substrate coverage, which can lead to non-uniform films and inconsistent properties. These limitations highlight the need for improved deposition control to achieve reproducible and high-quality thin films.

While Ti-doped ZnO thin films have been extensively studied using various techniques, there is limited investigation into how enhanced process control during deposition influences film uniformity, morphology, and electrical performance. In particular, the role of digitally controlled spray pyrolysis systems, which enable precise regulation of deposition parameters (e.g., flow rate, spraying intervals, and power input), has not been sufficiently explored in the context of Ti-doped ZnO thin films.

Therefore, this study employs a digitally controlled spray pyrolysis technique to deposit Ti-doped ZnO thin films and systematically investigate the effect of Ti incorporation on their morphological and electrical properties. The use of an automated and controlled deposition system is expected to improve film uniformity and reproducibility, thereby providing deeper insight into the relationship between doping concentration, microstructure, and electrical performance for photovoltaic applications.

MATERIALS AND METHODS

Digital Controlled Spray Pyrolysis Technique

In this investigation, a spray pyrolysis approach was developed and digitally controlled using an automation equipment for spraying. The digitally controlled device (DCD) was made up of three main sections. The sections are the switching sections, the power section, and the automation section. The heartbeat of the three sections was a microprocessor which is Atmega328P. A programmed code through which the microprocessor worked was written using Arduino IDE and transferred into the controller through a USB to TTL (FT232RL) adapter. The momentary switch function when press transmits a signal to the switching section's relay, to initiate a spraying command. The LED in the circuit served as an indicator thereby lights for around a minute after blinking during each spraying time when the spraying cycle is finished. The automation section comprised of resistor, crystal oscillator, capacitors, as well as Atmega328P.

The switching section is made up of a switching transistor (2N2222), DC relay, and a resistor. The gadget gets a signal from the automation section, routes it through the resistor to the transistor's base, and then on the relay, thereby empowering the fuel pump and spray nozzle for a set period of time.

A 12V/7Ah battery was utilized by the power section to powers the complete circuit. When the relay is turned on, the battery powers the fuel pump as well as the spraying nozzle, the automation section receives 5V from LM 7805. The fuel pump's motor run at a volume flow rate of 4.60 ml/s, spray 0.92 ml every 0.20 seconds, and pause for 30 seconds so as to have a dry, neat, and even spraying. More so, to allow total adherence of the precursors to the substrate. The fabricated spray pyrolysis device used allowed full control of the deposition parameters used in this work.

Figure 1 shows the circuit diagram of the digital control device.

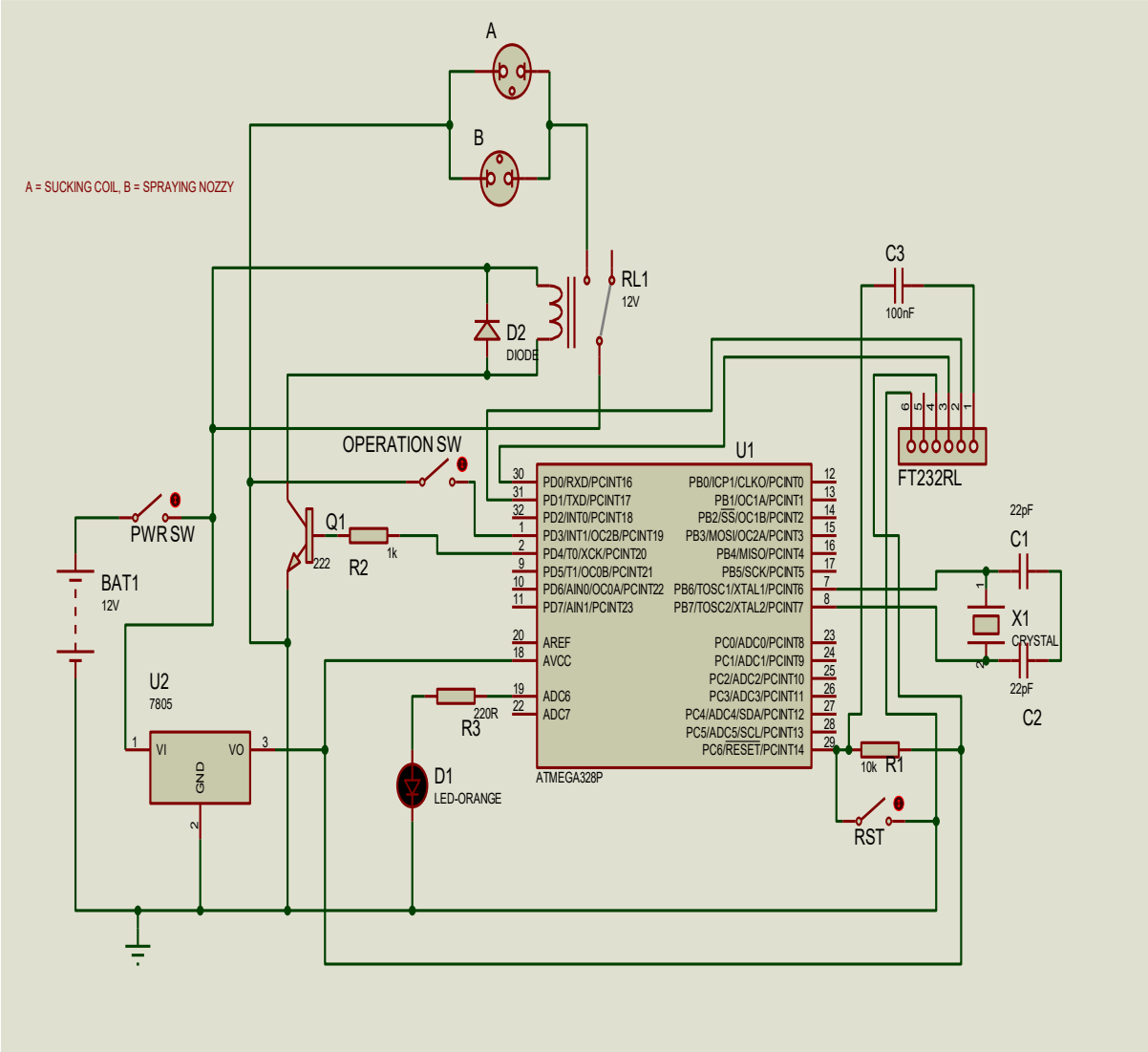


Figure 1: Circuit diagram of the digital control device

Materials

The flat indium tin oxide (ITO) substrate was employed in this investigation. The liquid precursors for the films were made from titanium dioxide (TiO_2), high quality zinc acetate (Zn $(CH3COO)_2.2H_2O$), and distilled water. Owoeye *et al.* (2019) chose zinc acetate above other precursors because of its multiple advantages.

Zinc Acetate Precursor

ZnO thin films precursors were obtained using pure Zinc acetate with the formula (Zn $(CH_3COO)_2.2H_2O$). The precursor was prepared in distilled water at 0.2 molar. 2.195 g of zinc acetate was dissolved in 50 ml of distilled water so as to obtain 0.2 M of zinc acetate precursor.

Precursor for Titanium Dioxide

To adjust the concentration of metal components in the films so as to achieve specific properties such as electrical conductivity and morphology of the films, the precursors were generated at 0.2M using distilled water. Hydrogen peroxide was subsequently added to facilitate the oxidation of titanium species, promoting the formation of TiO_2 during the deposition process.

Ti-doped ZnO Precursor

To create the Ti-doped ZnO thin films, the precursors were combined in a mixture of Titanium Dioxide 0 to 10% by volume of Zinc acetate. This was done for titanium dioxide precursors of 3%, 6%, and 9%, as well as zinc acetate precursors of 97%, 94%, and 91%. Initially, 1.5 ml of TiO_2 precursor was put into 48.5 ml of Zn $(CH_3COO)_2.2H_2O$ precursor in order to have 97% zinc acetate with 3% titanium dioxide respectively. The same procedure was utilized to obtain 6% Ti doped ZnO and 9% Ti doped ZnO. The resulting precursors underwent thorough stirring before spraying of the

already heated ultrasonically cleaned substrates. In this work, the precursors were prepared using the same techniques as in previous studies (Owoeye *et al.,* 2021). The reaction mechanism of the mixture is shown in Equation 1.

$$T_iO_2 + H_2O_2 + \ Zn(CH_3COO)_2.2H_2O \xrightarrow{\Delta,350\ ^\circ C} Ti - ZnO + 3CO_2 \uparrow + CH_4 \uparrow + 3H_2 \uparrow + H_2O \uparrow + O_2 \uparrow \quad (1)$$

The sample code and precursor amount for ZnO as well as Ti-doped ZnO fluids are shown in Table 1.

The prepared precursors were deposited on pre-heated ITO glass substrates by the invented digitally controlled spray pyrolysis device. The prepared Zinc Acetate precursor ($Zn\ (CH_3COO)_2.2H_2O$), Titanium Dioxide (TiO_2), and Ti-doped ZnO solutions were thoroughly mixed before spraying on pre-heated ultrasonically cleaned ITO glass substrates at a temperature of 350 °C. This temperature was monitored using a thermocouple thermometer. The distance between nozzle and substrate in this experiment was 45 cm.

Table 1: Samples, and its corresponding precursor amount

Sample Name	Precursor solutions
T0	100% ZnO (Control)
T1	97% ZnO with 3% Ti
T2	94% ZnO with 6% Ti
T3	91% ZnO with 9% Ti

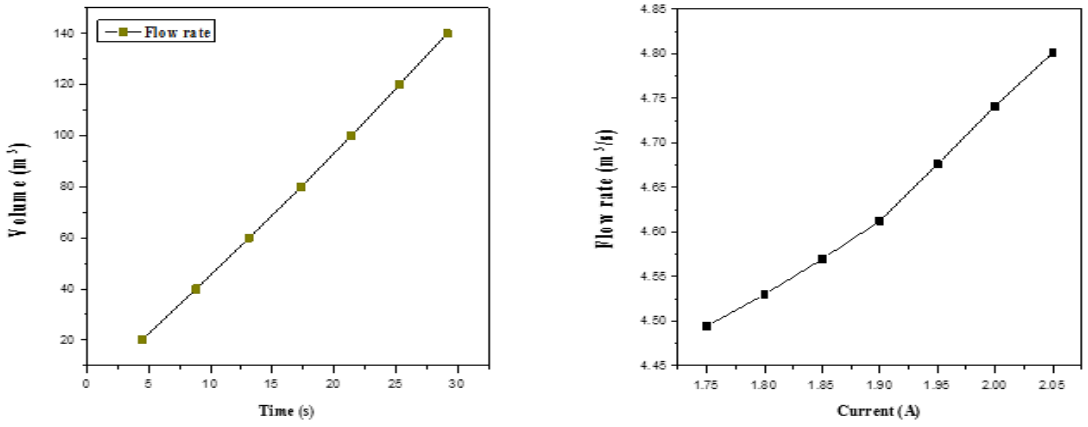
Characterization

The thin films of ZnO as well as Ti-doped ZnO were examined utilizing Scanning Electron Microscope (SEM), (JEOL JSM-7600F). The SEM was calibrated according to the manufacturer's specifications prior to imaging. Also, the films' morphology and elemental composition was obtained with Energy Dispersive X-ray Spectroscopy (EDX). The films' electrical characteristics, (I–V) was evaluated with the aid of Keithley Source Meter 4-point probe method. The measurement uncertainty was estimated to be within ±2% based on instrument resolution and experimental conditions.

RESULTS AND DISCUSSION

Volumetric flow rate of precursors

Water flow experiments were conducted to determine the flow rate of the designed spray pyrolysis equipment by measuring the volume of fluid flowing per unit time. The amount of time required for 20 ml volume to flow was recorded. The timing was determined at a constant voltage of 12 volts and varying currents. An average value of 4.60 ml/s was deduced as the flow rate. For this study, 4.60 ml/s was utilized to program the amount of ZnO as well as ZnO with doped Ti sprayed on the prepared substrate. Figure 2(a) illustrates the flow rate of the precursors while Figure 2(b) shows the variation of flow rate with current.



(a) (b)

Figure 2: (a) Flow rate of the precursors (b) Flow rate against current.

The samples' morphological properties

Images of the thin films of sample T0 – T3 are shown in Figure 3. The films have excellent substrate adherence and were dispersed uniformly throughout the substrate surfaces without any defects namely; voids, cracks, and so on. According to Olumurewa *et al. (2022) it has* a better performance. The micrograph of T0 thin film showed that there are many grains in its structure. However, there seems to be some conglomeration of the grains due to the increment in crystal size of T0 with doped Ti atoms. The micrographs reveal polycrystalline nature when doped with Ti atoms.

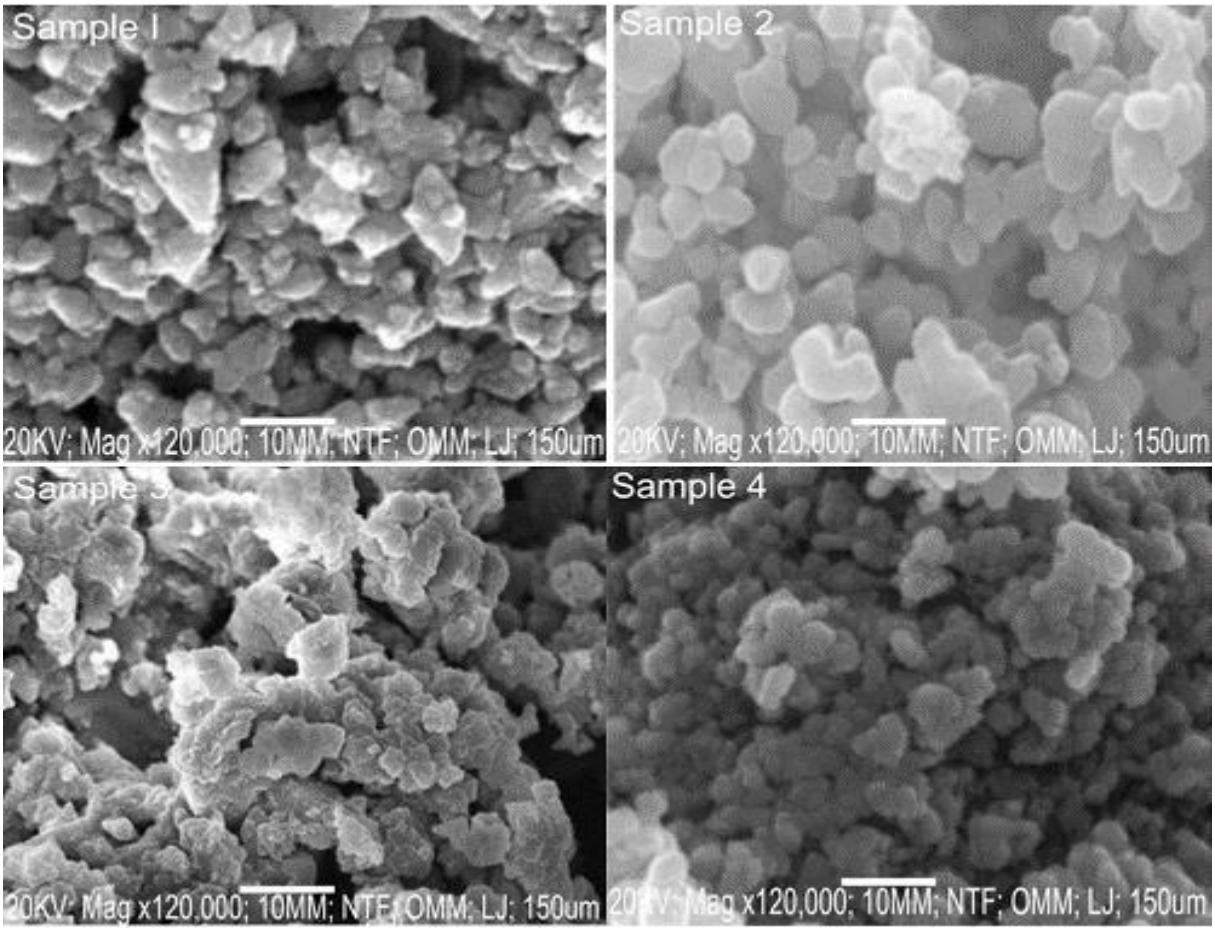


Figure 3: SEM micrograph of Sample: (1) T0 (2) T1 (3) T2 and (4) T3

Figures 3 compared the morphology of T0 thin film to T1, T2 and T3 thin films. An improvement in the samples surface characteristics was observed owing to an increase in the amount of dopant level (Ti). Homogeneity and surface adherence were observed in the deposited nanostructure as a result of a favorable growing environment (Ajenifuja *et al.,* 2015).

According to previous reports, degenerate ZnO causes heavy and localized grain nucleation to occur. When there was an increase in ZnO dopant amount, it was noticed that the number of nucleation sites increased (Kaur *et al.,* 2015). Cracks were absent in the SEM micrographs of this study has compared to the study of Khan *et al.* (2016).

Samples' Elemental Composition

The EDX depicts certain chosen spots on the SEM micrograph which are shown in the EDX spectra in figure 4. The compositional peaks of samples T0, T1, T2, and T3 are illustrated in Figures 4.

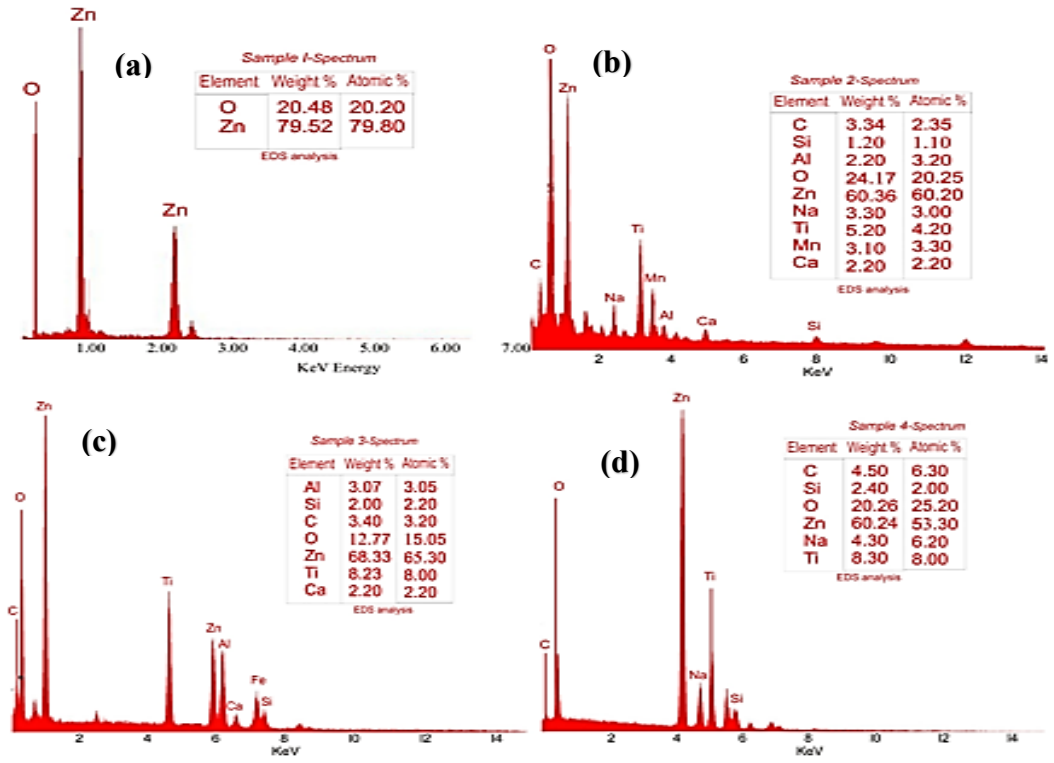


Figure 4: EDX of samples: (a) T0 (b) T1 (c) T2 (d) T3

Table 2 reveals the effect of Ti doping on the element present in ZnO thin films. The major elements in sample T0 are found in the proportions of Zn = 79.52 % and O = 20.48 %. For the thin films of ZnO with doped Ti, the composition in T1 was determined in the proportion of Ti = 5.20%, Zn = 60.36%, and O = 24.17%. Additionally, thin films of T2 are found in proportions of Ti = 8.23%, Zn = 68.33%, and O = 12.77% and finally T3 in the proportion of Ti = 8.30%, Zn = 60.24% and O = 20.26% respectively.

Table 2: Effect of Ti Doping on the Elements present in ZnO Thin Films

Samples	Ti (%)	Zn (%)	O (%)	Si (%)	C (%)	Others (%)
T0	-	79.52	20.48	-	-	-
T1	5.20	60.36	24.17	1.20	3.34	5.73
T2	8.23	68.33	12.77	2.00	3.40	5.27
T3	8.30	60.24	20.26	2.40	4.50	4.30

The EDX results confirmed that Ti, Zn, and O existed in the films samples. The presence of other elements in the EDX result may be due to the impurities that emanated during deposition or characterization.

The EDX graph confirmed the enlargement of Ti content in samples T1 – T3 thin films. Additionally, it was noted that the thin films' oxygen content dropped from 20.48% in T0 to 20.26% in T3. It is possible that contaminants that may have been produced in the structure during deposition are the cause of the oxygen's inability to remain stable when the Ti level in the Ti-doped ZnO film rises. It is evident that the percentage (%) composition of Ti calculated on the ITO glass substrate progressively grew from 5.20 to 8.30% as Ti concentration increased. Elemental composition analysis result obtained by Sridhar *et al.* (2013) indicated that Ti, Zn, and O existed in the films. Their results agree with the outcome of this study.

Electrical properties

The I-V characteristics based on measurements made using a 4-point probe showed noticeable current and voltage curve changes for samples T0, T1, T2 and T3 thin films. When it comes to the I-V features, as shown in figures 5 (a-b), the films showed an increase in current as the doping level increased. The increase in the current of T0 when doped with Ti atoms may also be due to an increase in T0 crystal population with dopant. However, as the doping concentration of Ti increased in T0, there is a corresponding increase in the current as shown in the I-V curve.

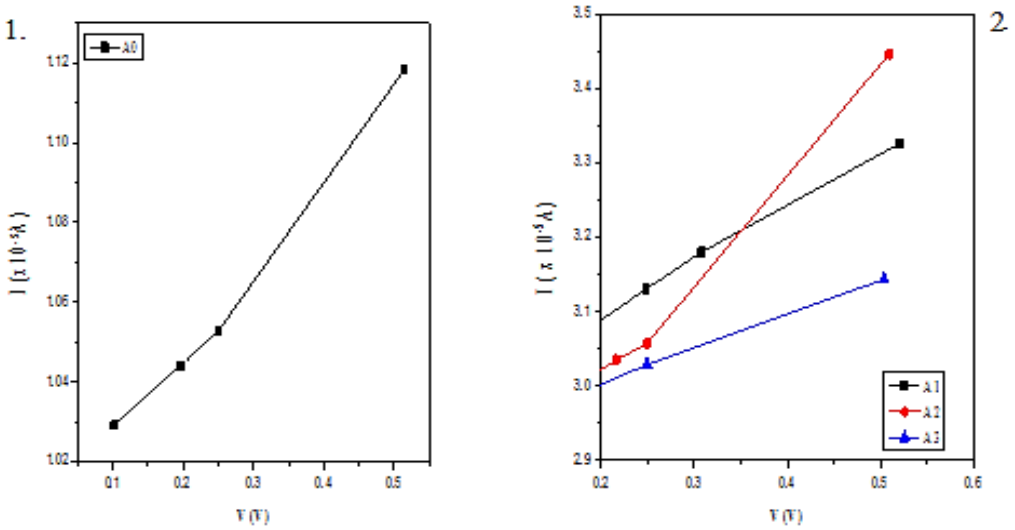


Figure 5: I – V characteristics for T0 (a) and T1 –T3 (b)

A linear characteristic was seen by Sridhar *et al.* (2013) for Ti-doped ZnO thin films while the resistance of the film was deduced from the slope of the graphs. As Ti concentration rose, the films' resistivity decreased due to an increase in free electrons in the film. Positive Ti_{Zn} charges were produced in the substance as a result of Zn^{2+} ions being replaced by Ti^{4+} ions within the crystal lattice. In the findings of Rajasekaran *et al.* (2020) on ZnO with doped Ti, it showed that ZnO with doped Ti conductivity increased as the doping level increased, with 6% Ti-doped ZnO having the highest conductivity. This study aligns with the above. Table 3 shows the values gotten from the electrical measurement which suggests possible applicability in photovoltaic systems.

Table 3: Effect of Ti Doping on the Electrical properties of ZnO Thin Films

Samples	Thickness (nm)	Sheet Resistance, Rs (× 10^3 Ω/sq)	Resistivity, ρ (x 10^{-3} Ω·m)	Conductivity, σ (× 10^2 S/m)
T0	280	5.80	1.62	6.17
T1	320	4.90	1.57	6.37
T2	350	3.80	1.33	7.52
T3	300	4.50	1.35	7.41

CONCLUSION

Undoped ZnO as well as ZnO doped with Ti thin films were successfully sprayed on ITO glass substrate by a specially designed digital spray pyrolysis technique. SEM and EDX findings reveal that Zn, Ti, O, ZnO, and Ti-doped ZnO existed in the films. As the quantity of Ti dopant was increased, the ZnO films' surface shape and microstructure improved. The I-V characteristics showed a reduction in ZnO resistance with Ti doping having a conductivity value of $7.52 \times 10^2\ S/m$ at 6% Ti-doped ZnO. At 6% Ti-doped ZnO thin films synthesized in this study showed good surface morphology and electrical properties suggesting possible applicability in photovoltaic systems.

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