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# THE OPTOELECTRONIC CHARACTERIZATION OF Ag DOPED ZnO THIN FILMS

**Serif RUZGAR**

*Batman University, Vocational School of Health Services, Department of Opticianry Program, Batman, Türkiye, serif.ruzgar@batman.edu.tr*

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## ABSTRACT

This study investigates the properties of silver (Ag)-doped zinc oxide (ZnO) thin films, which possess significant potential for various optoelectronic applications. The films were fabricated utilizing a cost-effective nebulizer spray technique. Structural analysis confirmed that both the undoped and Ag-doped samples crystallized in the hexagonal wurtzite phase, characteristic of ZnO. Scanning electron microscopy (SEM) revealed that the incorporation of Ag significantly altered the surface morphology, resulting in an increased grain size and the formation of more irregular surface features. Optical measurements demonstrated that while Ag doping slightly reduced the films' transmittance, it concurrently narrowed the optical band gap, thereby enhancing light absorption within the visible region. Moreover, the photoluminescence characteristics were observed to be strongly dependent on the presence of the silver dopant. Finally, current-voltage (I-V) characterization affirmed that the Ag-doped ZnO films exhibited superior photoconductivity compared to their undoped counterparts. An evaluation of the photodetector performance parameters indicated a substantial improvement in photosensitivity, which increased from a value of 14.7 in undoped ZnO to 64.2 following the incorporation of Ag.

## 1. INTRODUCTION

ZnO thin films represent a key material in the development of photodetectors and other optoelectronic devices due to their favorable intrinsic properties. ZnO possesses a wide direct band gap (≈3.37 eV) and a high exciton binding energy (≈60 meV) at room temperature, enabling excellent performance in ultraviolet (UV) and visible-light optoelectronic applications [1-2]. In addition, its non-toxic nature, high transparency, and superior chemical and thermal stability make ZnO an environmentally friendly and durable semiconductor material [3-4]. These characteristics have led to its extensive use in UV photodetectors, laser diodes, LEDs, and piezoelectric devices [5-6]. However, the ZnO thin films exhibit several limitations, including high electrical resistivity, photocorrosion under UV exposure, and limited photoresponse in the visible spectrum [7-9]. To address these challenges, doping ZnO with appropriate metallic or nonmetallic elements has become an effective strategy to tailor its electronic structure and enhance its optoelectronic performance [10-11]. Doping introduces new energy levels within the band gap, thereby modifying carrier dynamics, conductivity, and light absorption properties. Among different dopants, Ag has attracted significant attention due to its amphoteric character, allowing Ag atoms to occupy both substitutional and interstitial lattice positions within the ZnO crystal structure [12]. This unique behavior introduces donor and acceptor energy levels near the conduction and valence bands, effectively improving carrier generation and recombination processes [13]. Previous studies have reported that moderate Ag incorporation enhances photoconductivity, photosensitivity, and visible-light absorption without severely disturbing the wurtzite ZnO structure [14-15]. Nevertheless, the detailed effects of Ag doping concentration on the structural, morphological, and photoelectrical properties of ZnO films remain not fully understood—particularly for films synthesized via low-cost, solution-based deposition techniques.

In this study, Ag-doped ZnO thin films were synthesized using the nebulizer spray technique, a simple, scalable, and cost-effective method suitable for large-area thin film fabrication. This technique offers a promising alternative to vacuum-based deposition processes by enabling fine control over film thickness and uniformity at relatively low temperatures. The main objective of this work is to investigate how Ag incorporation influences the crystallinity, surface morphology, optical band gap, and photoconductivity of ZnO thin films, and to evaluate their potential as photosensitive materials for optoelectronic applications. Unlike many previous reports, this study provides a comprehensive characterization of Ag: ZnO films prepared via a low-cost nebulizer spray route, highlighting both the advantages of this synthesis approach and its potential impact on the development of high-performance, cost-efficient photodetectors.

## 2. MATERIAL AND METHOD

Undoped and 3 wt% Ag-doped ZnO thin films were synthesized on glass substrates using a nebulizer spray pyrolysis technique. High-purity zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and silver nitrate ($AgNO_3$), procured from Sigma-Aldrich, were used as the zinc and silver precursors, respectively. The undoped precursor solution was formulated by dissolving 0.1 M of zinc acetate dihydrate in distilled water under vigorous magnetic stirring until a clear, homogeneous solution was obtained. To prepare the doped precursor, a silver concentration of 3 wt% was introduced into the zinc acetate solution, which was then stirred for an additional hour to ensure uniform dispersion. The thin films were deposited using a Nano Mist nebulizer spray device. This device operates by ultrasonic atomization, generating fine droplets without the need for any carrier gas. The mist was sprayed toward the preheated substrate from a fixed distance of 5 cm at 450 °C. Each spray lasted about 2–3 s, with 30 s intervals between sprays, and the total deposition time was approximately 20 min. The Ag doping concentration was fixed at 3 wt% to achieve an optimal balance between improved optoelectronic performance and structural stability. According to previous studies, low-to-moderate Ag concentrations (1–5%) significantly enhance the electrical conductivity and photosensitivity of ZnO thin films without disturbing their wurtzite crystal structure or causing phase segregation. When the Ag content exceeds approximately 5 wt%, Ag atoms tend to aggregate or form metallic clusters on the film surface, which can generate defect-related states, reduce optical transparency, and degrade the photoconductive properties of the material. Conversely, very low concentrations (<1 wt%) do not lead to meaningful improvements in carrier density or optical bandgap modulation. Therefore, the 3 wt% doping level used in this study was selected as an optimum value that enables efficient incorporation of Ag atoms into the ZnO lattice while preserving the structural and optical quality of the thin films. Similar doping levels have been successfully employed in prior research on Ag-doped ZnO thin films for UV photodetectors and optoelectronic devices [16-18]. Prior to deposition, the glass substrates were subjected to a meticulous cleaning regimen involving a detergent wash followed by sequential rinsing with ethanol and distilled water to eliminate any surface contaminants. During the deposition process, the substrate temperature was precisely maintained at 450°C. Following deposition, silver paste was applied to the surface of the thin films to establish ohmic contacts for electrical measurements. The structural properties and phase purity of the fabricated films were investigated using a Bruker D8 Advance X-ray diffractometer (XRD), with diffraction patterns recorded over a 2θ range of 20°–60°. The optical characteristics of the films were evaluated across the 300–1000 nm wavelength range with a SOIF UV-5100H UV-visible spectrophotometer. Finally, the current-voltage (I-V) characteristics of the devices were measured using a Keithley 4200 semiconductor parameter analyzer under both dark conditions and various illumination intensities to assess their photoresponse.

## 3. RESULTS AND DISCUSSION

Figure 1 presents the X-ray diffraction (XRD) patterns of both undoped and Ag-doped ZnO thin films. The diffraction peaks observed at the (002), (101), and (102) planes, in alignment with the XRD patterns of ZnO (JCPDS No. 36-1451), are characteristic of the wurtzite hexagonal phase of ZnO. An additional diffraction peak observed at around 31.7° corresponds to the (100) plane of the hexagonal wurtzite ZnO structure. The slight variation in its intensity and position compared to the undoped sample may be attributed to lattice strain or minor structural distortion caused by the incorporation of Ag ions into the ZnO lattice. These peak positions are in good agreement with standard reference data [19]. Notably, no additional peaks corresponding to impurities or secondary phases, such as Ag-oxides or other Ag-based compounds, were detected. This suggests that, at the doping concentration used, Ag species are either incorporated into the ZnO structure in low concentrations or present as very fine clusters, below the XRD detection threshold. As a result, the films retain the wurtzite ZnO crystal structure. Moreover, while no significant shift in the peak positions was observed upon Ag doping, notable changes in the peak intensities were evident, implying alterations in crystallinity or preferred orientation. The full width at half maximum (FWHM) values further reveal a trend consistent with the level of Ag doping, indicating a reduction in crystallinity and crystallite size. The observed broadening of the FWHM values serves as clear evidence of the decrease in crystallite dimensions. Based on the FWHM values of the (101) diffraction peak, the average crystallite size was calculated using the Scherrer equation as approximately 26 nm for ZnO and 20 nm for Ag:ZnO. The reduction in crystallite size after Ag doping suggests that Ag incorporation slightly inhibits grain growth and introduces lattice strain within the ZnO structure [20]. Figure 2 (a) displays the transmittance spectra of both ZnO and Ag-doped ZnO thin films deposited on glass substrates via spray pyrolysis. Both films exhibit high transmittance in the visible spectrum, with the undoped ZnO film demonstrating slightly higher transmittance values. The average optical transmittance in the visible range (400–800 nm) decreased from about 85% for the undoped ZnO to 78% for the Ag:ZnO film. This suggests that Ag doping results in a slight reduction in optical transparency, likely due to increased light scattering and absorption associated with defect states [15]. Additionally, the absorption edge of the Ag-doped film shifts toward longer wavelengths compared to the pure ZnO film. This shift is indicative of Ag incorporation into the ZnO lattice, leading to the formation of new states within the band gap and a narrowing of the band gap.

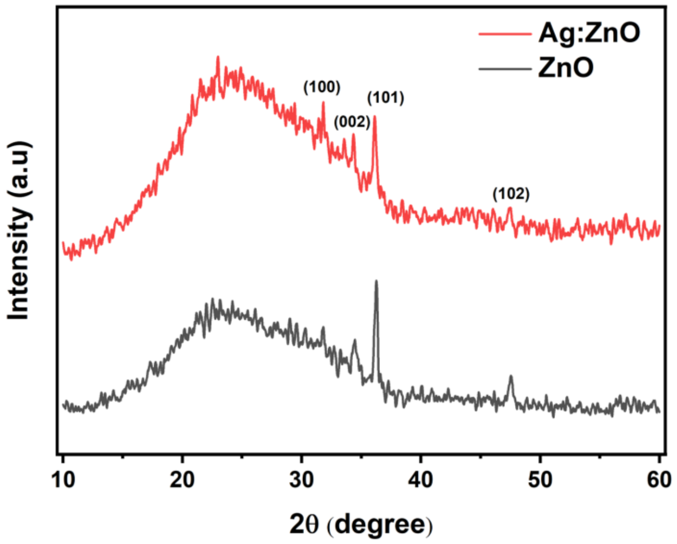

*Figure 1. XRD pattern of the ZnO and Ag: ZnO thin films*

Such a red shift enhances visible-light absorption, which can be particularly beneficial for photocatalytic and optoelectronic applications. The optical band gap values of the ZnO and Ag-doped ZnO thin films were determined using the Tauc relation; $(ahv)^2 = A(hv - Eg)$ , where Eg is the optical band gap energy. As shown in the newly added Tauc plots (Figure 2 (b)), the estimated band gap values are 3.26 eV for ZnO and 3.29 eV for Ag: ZnO. The slight increase in the band gap after Ag incorporation may be attributed to Burstein–Moss band filling, which occurs due to the rise in carrier concentration caused by Ag doping [21-23]. The observed band gap narrowing in the Ag-doped ZnO film facilitates the absorption of a broader range of visible photons, thereby generating more photo-induced charge carriers under illumination. This enhanced light–matter interaction improves photoconductivity and contributes to higher photosensitivity in photodetector applications. Thus, the band gap narrowing observed in Figure 2 can be considered advantageous for improving the overall photoresponse efficiency of the device.

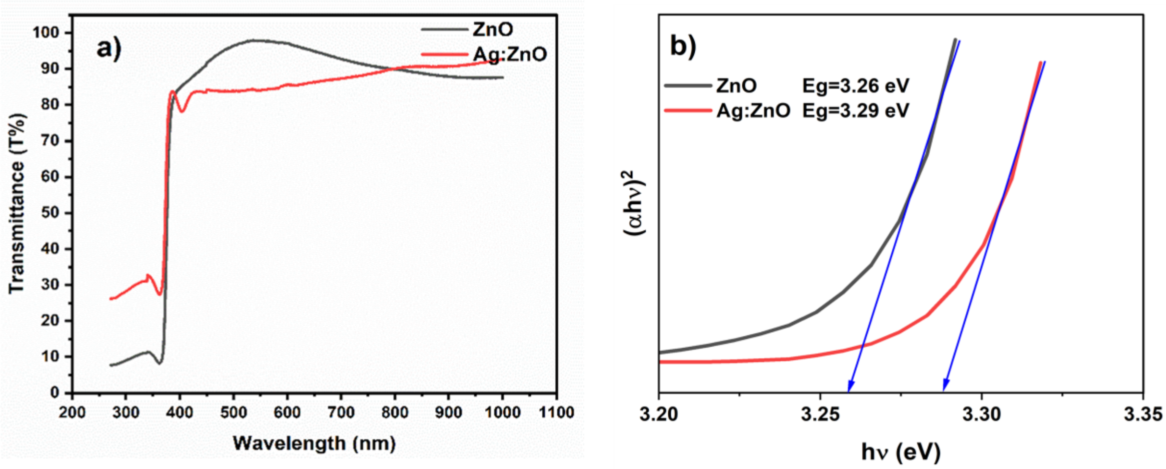

*Figure 2.* a*) Transmittance spectra and b) Tauc plot of the ZnO and Ag: ZnO thin films*

Figure 3 illustrates the scanning electron microscopy (SEM) images of ZnO and Ag-doped ZnO thin films fabricated on glass substrates using the nebulizer spray technique. The pristine ZnO film (Figure 3a) displays a relatively uniform surface morphology characterized by distinct granular structures with well-defined grain boundaries and a homogeneous distribution. In contrast, the Ag-doped ZnO film (Figure 3b) reveals pronounced modifications in surface morphology. The incorporation of Ag leads to a slight increase in grain size and induces irregularities in the surface texture. The appearance of lumpier or agglomerated features suggests that Ag incorporation may alter the ZnO crystal growth dynamics or promote the formation of Ag-related nanoparticles on the film surface. Such morphological variations are likely to have a direct influence on the optical and electrical behavior of the thin films. Figure 4 shows the room-temperature photoluminescence (PL) spectra of ZnO and Ag-doped ZnO thin films. Both samples exhibit emission features in the ultraviolet (UV) and visible regions. The UV emission corresponds to near-band-edge (NBE) recombination of electron–hole pairs in ZnO and is strongly associated with the material's crystallinity. In contrast, the visible emissions are generally linked to intrinsic structural defects within the lattice, such as oxygen vacancies ($V_o$), zinc interstitials ($(Zn_i)$), or zinc vacancies ($(V_{zn})$) [24-26]. The emission spectrum of the pure ZnO film is dominated by a sharp ultraviolet peak at 389 nm, alongside a distinct, broad luminescence across the visible range [27]. Upon silver incorporation, a significant quenching of the near-band-edge (NBE) ultraviolet emission is observed in the photoluminescence spectrum, accompanied by a pronounced alteration of the deep-level emission (DLE) band in the visible region.

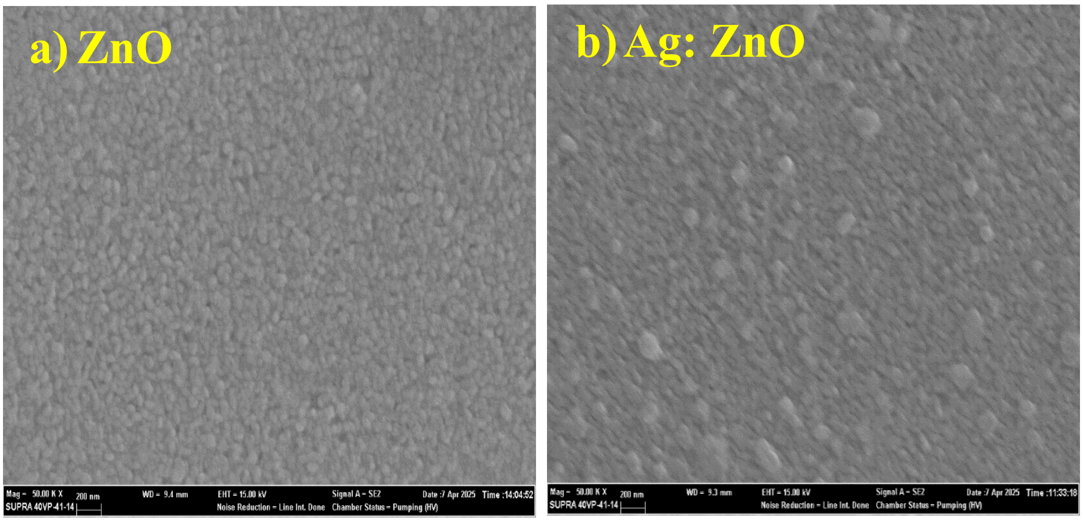

*Figure 3. SEM images of the ZnO and Ag: ZnO thin films*

The suppression of the NBE peak indicates that Ag dopants introduce energy levels within the ZnO bandgap that serve as non-radiative recombination centers, effectively creating an alternative pathway that competes with the radiative recombination of excitons. Concurrently, the modification of the visible luminescence profile suggests that Ag doping alters the native defect chemistry of the host lattice, either by creating new Ag-related radiative states or by changing the concentration of intrinsic defects. Collectively, these spectral changes demonstrate that silver doping profoundly modifies the electronic structure and charge carrier recombination dynamics within the ZnO material, thereby governing its optical properties. The modification of the PL spectra with Ag doping, particularly the suppression of the NBE peak and the enhancement of deep-level emissions, reflects the creation of Ag-related defect states within the ZnO band structure. These defect states can trap photogenerated carriers, thereby reducing their recombination rate and extending carrier lifetime. As a result, the Ag-doped ZnO films exhibit improved charge separation and enhanced photosensitivity under illumination. This strong correlation between the PL behavior and the electrical response confirms that the incorporation of Ag plays a beneficial role in optimizing the optoelectronic performance of ZnO-based photodetectors.

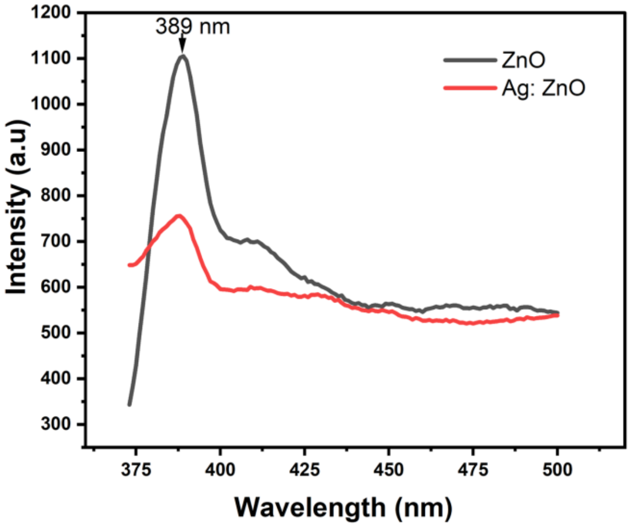

*Figure 4. PL spectra of the ZnO and Ag: ZnO thin films*

Figures 5 (a)–(b) presents the current–voltage (I–V) characteristics of the ZnO and Ag-doped ZnO thin films measured in the dark and under various illumination intensities. While the ZnO film exhibits a low current value in the dark, a significant increase in current is observed as the light intensity increases. This clearly demonstrates the photoconductive properties of ZnO. Light absorption causes the formation of electron-hole pairs from the valence band to the conduction band, which increases the free carrier concentration and thus increases the electrical conductivity. The nonlinear increase in current with voltage may indicate the presence of potential barriers or contact resistances in the film. The I-V characteristics of the Ag-doped ZnO film show significant differences compared to the pure ZnO film. The nonlinear behavior observed in the I–V curves (Figure 5) can also be attributed to the formation of a Schottky barrier at the metal/semiconductor interface. In Ag/ZnO contacts, a potential barrier arises due to the difference in work functions between Ag and ZnO, which governs the charge transport across the junction. Under illumination, the barrier height is partially lowered as photogenerated carriers accumulate at the interface, reducing the depletion region width and facilitating carrier transfer. This modulation of potential under light exposure supports the Schottky-type conduction mechanism and explains the observed enhancement in photocurrent. The Ag doping appears to affect both the dark current and the photocurrent. In general, it can be observed that Ag doping increases the photoconductivity of the material, as under the same light intensity, the Ag-doped film can exhibit higher current values. This increase can be explained by Ag creating new energy levels within the ZnO lattice, contributing to the generation of more carriers, or by improving the material's light absorption ability. Furthermore, Ag doping can also alter carrier mobility by affecting the film's surface morphology and grain boundaries. This photoconductivity increase enhances the potential of Ag-doped ZnO for photodetectors and other optoelectronic applications. The photodetection performance of the fabricated photodetectors was evaluated in terms of photosensitivity (P), photoresponse (R), and specific detectivity (D). From the photocurrent spectra, these parameters of the sensors were determined by using the following equations [28-29]:

$$P = \frac{I_{ph} - I_{dark}}{I_{dark}} \tag{1}$$

$$R = \frac{I_{ph}}{P_{in} \times A} \tag{2}$$

$$D = R\sqrt{\frac{A}{2eI_{dark}}} \tag{3}$$

wherein the terms $I_{ph}$, $I_{dark}$, A, $P_{in}$, and e correspond to the photocurrent, dark current, device active area, incident illumination intensity, and elementary electron charge, respectively. The calculated optoelectrical parameters are given in Table 1. When the effect of Ag doping on the photodetector properties of ZnO thin films was investigated, remarkable results were obtained. While the photosensitivity was 14.7 in the undoped ZnO film, this value increased to 64.2 with Ag doping. This increase can be explained by the fact that Ag atoms reduce the dark current, thus increasing the current difference between light and dark. However, a significant decrease was observed in the photoresponse, decreasing from 1.53 A/W to 0.24 A/W. This may be due to the Ag doping reducing the photocurrent efficiency by impeding carrier transport. However, there was no significant deterioration in the detectivity value; only a small decrease was observed. These results indicate that Ag doping is effective in increasing photosensitivity but limits the photoresponse. Therefore, Ag-doped ZnO films are advantageous in applications requiring high contrast and low dark current, while undoped ZnO films appear more suitable for applications requiring high photoresponse. Moreover, the contrasting trends in photosensitivity and photoresponse presented in Table 1 can be explained by the combined effects of Ag-induced defect states and interfacial barrier modulation. The significant increase in P indicates that Ag incorporation effectively suppresses the dark current, thereby amplifying the relative current difference between illuminated and dark conditions. However, the concurrent decrease in R suggests that carrier transport is partially hindered by defect-related recombination or potential barriers at the grain boundaries. In this case, Ag acts both as a sensitizing agent that enhances photocarrier generation and as a scattering or trapping center that limits carrier mobility.

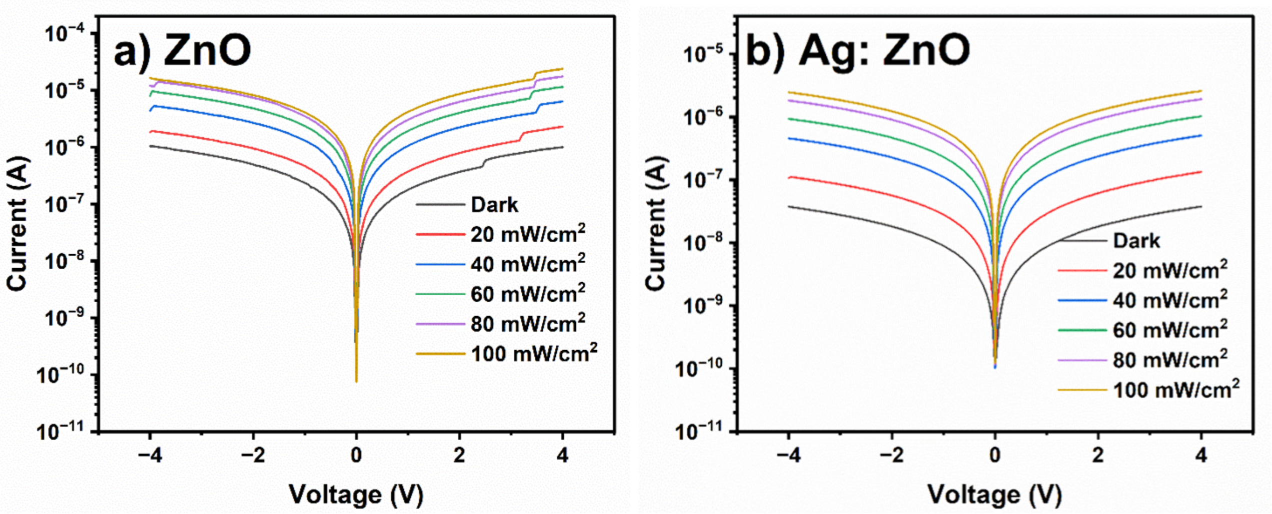

*Figure 5. The I-V characteristic of glass/ZnO/Ag and glass/Ag: ZnO/Ag photosensor under dark and various illumination intensities*

Therefore, while Ag doping improves the photodetector's contrast and stability by lowering leakage current, it simultaneously restricts its absolute photoresponse due to increased recombination losses.

The significant improvement in photosensitivity observed in Ag-doped ZnO thin films indicates that controlled Ag incorporation can effectively enhance the photodetection capability of ZnO-based devices. The reduction in dark current and improved contrast ratio suggest that these films are particularly suitable for low-light or UV sensing applications, where signal-to-noise ratio is critical.

*Table 1. The optoelectrical parameters of ZnO and Ag: ZnO*

| | **P** | **R (A/W)** | **D(jones)** |
|---|---|---|---|
| **ZnO** | 14.7 | 1.53 | $2.65\times10^{10}$ |
| **Ag: ZnO** | 64.2 | 0.24 | $2.20\times10^{10}$ |

Furthermore, the use of a cost-effective nebulizer spray deposition technique provides an attractive route for scalable fabrication of large-area, transparent, and flexible photodetectors. These features make Ag-doped ZnO thin films promising candidates for integration in next-generation optoelectronic devices such as environmental UV sensors, optical communication systems, and wearable photodetectors. Thus, the present study demonstrates both the scientific and technological potential of Ag doping in ZnO for practical optoelectronic applications.

## 4. CONCLUSION AND SUGGESTIONS

In this study, Ag-doped ZnO thin films were successfully synthesized using a cost-effective nebulizer spray pyrolysis technique, and their structural, optical, and electrical characteristics were systematically investigated to evaluate their potential for optoelectronic applications. The incorporation of Ag atoms slightly reduced the crystallite size and modified the surface morphology, leading to the formation of irregular grains and enhanced surface roughness. These structural and morphological changes contributed to improved light scattering and increased optical absorption, while the introduction of Ag-related states within the ZnO lattice resulted in a slight band gap narrowing, further promoting visible-light absorption. From the electrical characterization, it was found that Ag doping significantly enhanced the photoconductivity and photosensitivity of ZnO films while reducing the overall photoresponse. The most notable outcome of this work is the substantial enhancement in photodetector performance. The Ag-doped film exhibited higher photosensitivity than undoped ZnO, with values increasing from 14.7 to 64.2. The increase in photosensitivity can be attributed to the reduction of dark current due to defect passivation and Schottky barrier modulation at the Ag/ZnO interface, which enhances the contrast between illuminated and dark conditions. Conversely, the decrease in photoresponse arises from Ag-induced defect states that act as carrier traps, limiting charge mobility and increasing recombination losses. This interplay demonstrates how the structural and optical modifications induced by Ag directly affect the electrical response of the films. The nebulizer spray technique used in this work offers several advantages for device fabrication, including low processing temperature, excellent film uniformity, material efficiency, and scalability for large-area deposition. These features make it highly suitable for integrating ZnO-based thin films into cost-effective, flexible, and transparent optoelectronic components. Overall, the results confirm that controlled Ag doping is an effective approach to tuning the optoelectronic properties of ZnO thin films. The observed enhancement in photosensitivity, reduction in dark current, and improved contrast ratio highlight the potential of Ag:ZnO films for practical use in UV and visible photodetectors, optical communication systems, and other high-contrast, low-noise optoelectronic devices. Therefore, this study not only demonstrates the scientific significance of Ag incorporation in ZnO but also reinforces its technological promise for next-generation, low-cost, and high-performance photodetector applications.

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**Statement of Research and Publication Ethics**

The study is complied with research and publication ethics.

**Artificial Intelligence (AI) Contribution Statement**

This manuscript was entirely written, edited, analyzed, and prepared without the assistance of any artificial intelligence (AI) tools. All content, including text, data analysis, and figures, was solely generated by the author.

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