JOURNAL OF NANO AND MATERIAL SCIENCE RESEARCH
Volume 1 (Maiden edition, 2022), pp. 28-48
Available online at journals.nanotechunn.com/jnmsr

ORIGINAL ARTICLE

A Review on Microstructural, Optical, Electrical and Gas Sensing Properties of Aluminum-doped Zinc Oxide Thin Films for Gas Sensing and Optoelectronic Applications

Santus C. Onuegbu[a], S.S. Oluyamo[a] and O. I. Olusola[b]*

[a]*Department of Physics, Faculty of Science, Alex Ekwueme Federal University, Ndufu-Alike, P.M.B 1010, Ebonyi State, Nigeria*
[a,b]*Department of Physics, School of Science, The Federal University of Technology, Akure (FUTA), P.M.B. 704, Nigeria*

KEYWORDS

Al-doped zinc oxide,
Thin films,
Electrical properties,
Gas sensing properties,
Porous morphology

ARTICLE HISTORY

Received: May 30, 2022
Revised: June 28, 2022
Accepted: July 25, 2022

ABSTRACT

In recent years, Al-doped ZnO nanoparticles have been proven to be a promising transparent material applicable in the fabrication of varistors, gas sensors, and thermoelectric, piezoelectric, and electro-optical devices due to its high electrical conductivity and porous morphological nature. Doping ZnO with Al-ions has demonstrated to have strong impact on the overall properties of ZnO nanostructures and significantly improve the electronic performance of ZnO nanomaterial. However, this review summarizes the effect of Aluminium ions as a dopant on the structural, optical, and electrical and gas sensing properties of zinc oxide thin films. The study observed that the presence of aluminum ions in the ZnO film significantly improved the electronic and gas sensing properties of the films; yet it was remarkably noted from the assembled data that the structural quality of the AZO deteriorated heavily upon increasing the Al-dopants. The morphology of the Al-ZnO thin films was severely influenced, as the study showed that increasing the Al^{3+}/Zn^{2+} ratio transited the AZO films from hexagonal nanocrystalline into a porous mixture of nanosheets, nanorods, nanowires, narcissus, wrinkled and cluster structures. However, considering the desired morphology and phase purity, as well as enhanced electrical properties, gas sensing properties, and optical transmittance, the optimal window of Al^{3+}/Zn^{2+} ratio in the fabrication of Aluminium doped zinc oxide thin film was observed between 1at% and 6at%, beyond which the properties of the AZO as observed from the experimental data will no longer be suitable for optoelectronic and gas sensing applications. Further, the authors concluded the review with advancement, challenges, and recommendation for future improvement of Al-doped ZnO as a transparent material for optoelectronic and gas sensing applications.

1 Introduction

Transparent conductive oxide (TCO) thin films have been employed extensively as transparent electrodes in the fabrication of flat panel displays [1], solar cells [2-4], optoelectronic devices [5] and gas sensors [6]. However, In the area of solar cells application, the transparent conductive oxides are needed to satisfy certain conditions such as being strongly transparent in the visible region where the solar cell operates (in order to reduce the photon absorption), having high conductivity (as to reduce resistive losses) and also having a low carrier concentration (to reduce the absorption losses in red and near-infrared region) [7].

Over the past decades, the indium tin oxide (ITO) had dominated the commercial market as the most cherished transparent conductive oxides due to its strong optical and electrical conductivity and transparency in the visible region. The ITO films have shown some deficiencies such as general high fabricating cost and unsuitability for flexible devices. For instance, for large-area touch screens, the resistivity of ITO is very high for the quick touch sensing response; and indium tin

[*]**CORRESPONDING AUTHOR** | Onuegbu Santus | ✉onuegbus.c@yahoo.com

oxide is very brittle, and therefore appears insufficient for various applications in flexible electronics [8]. Therefore, is a need to develop new transparent materials that can solve the drawbacks associated with the ITO films.

These shortcomings associated with ITO have prompted the need to explore other alternative materials that can conveniently replace ITO films in electronic applications. In this respect, Aluminium-doped Zinc oxide (AZO) thin films has become the most promising alternative to ITO films due to its low fabrication cost and comparable electrical and optical characteristics. Al-doped ZnO thin films are known n-type semiconducting materials having a direct wide band gap energy (3.3 eV) and exhibiting a wurtzite crystal structure.

Further, Al-doped ZnO thin films offer a lot of advantages over ITO such non-toxicity and biocompatibility, low temperature fabrication route, easy scalability for large areas, high transmission in the near infrared region and high thermal and chemical stability [9-15]. All these interesting characteristics make AZO a choicest transparent conductive oxide for photovoltaic.

Interestingly, Al-doped ZnO thin films have recently been incorporated as a part of CdTe and $CuInSe_2$ solar cells, which have become the leading contender for practical large-scale photovoltaic systems [16-19]. Doping ZnO thin films has proven to sufficiently enhances the electrical and gas sensing properties of the AZO film [20-23]. The Al-doped ZnO thin films can be fabricated by various deposition techniques like Sol-gel [24], spray pyrolysis [25], thermal evaporation [26], pulsed laser deposition [27], DC and RF magnetron sputtering [28], atomic layer deposition, ALD [29] etc.

The properties of the Al-doped ZnO strongly depend on the method of deposition and other growth parameters. However, several experimental results have reported that the atomic layer deposition, sol-gel and spray pyrolysis produced the most uniformly aligned Al-doped ZnO thin films

In the present work, the authors summarize the effect of Aluminium dopant on the microstructural, optical, electrical and gas sensing properties of Al-doped thin film for application in optoelectronics and gas sensing.

2 Effect of Aluminium dopant on the structural and optical properties of ZNO (AZO) thin films

The structural properties of thin films play huge contributions on the overall performance of the thin films and greatly determine the suitability of the material for various applications.

Ideally the morphology of nanoparticles determines the applicability of the nanoparticles in various optoelectronic devices, solar cell applications, and other areas where nanoparticles are applied. However, understanding the influence of the dopant materials on the structure of thin films will offer the advantages of knowing the best area of application of the thin films.

C. H. Lee and D. W. Kim [30] prepared Al-doped ZnO thin films on soda lime glass substrate at 275°C by MOCVD using ultrasonic atomization to study the structural properties of the AZO thin films. Zinc acetylacetonate and aluminum acetylacetonate were used as the source of precursor of Zn and Al dopant, respectively. The study focus was on the effect of Al-doping concentration of 1at%, at%, 3at%, 4at%, 5at% and 6at% on the structural characteristics of AZO thin film; the result of the study showed that increasing the Al content enhances the crystal quality of the film. It was observed that at 6% concentration of aluminum, the AZO films had its best crystal quality and grain sizes, and density of the films were increased.

Additionally, the morphology of the films as revealed by the FE-SEM show that at low doping concentration especially below 6%, the films exhibited a consisting of columnar grains with faceted surface with significant number of pore and space within the grain boundary. This porous morphology also shows that the films can find application in gas sensing device.

However, as the concentration of the Al-ions increases beyond 4 at% in the matrix of ZnO, the surface of the films flattens with increased grain size and the pores initially observed disappeared. The authors did not give a cogent reason for the disappearance of the pores upon higher Al doping, because it is expected that the pore and other defects in the films will increase at large Al doping content.

The broadness seen in the XRD pattern of the AZO thin films with increasing Al-ions concentration supports the possibility of increase in number of pores in the films, which the authors could not give account of it in their morphology results. The XRD patterns of the AZO for different doping concentrations can be seen in the figure 1. The Figure 1 shows that at higher doping concentration of the Al-ions, the diffraction peaks of the following planes (101) and (102) became much weakened; suggesting that large Al-doping favors the growth of the films along the C-axis direction.

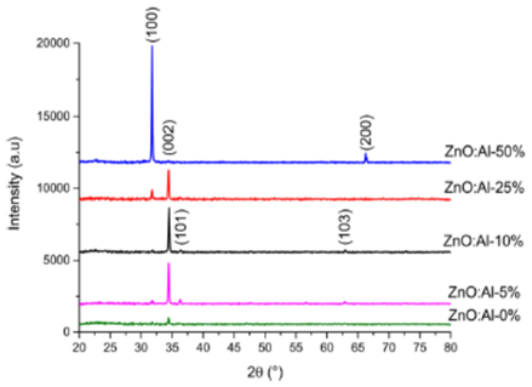

Figure 1: XRD patterns of the AZO thin films with different Al-doping concentrations of a) 0 at%, b) 5 at%, c) 10 at%, d) 25 at%, and e) 50 at%

Speak [31] reported the influence of aging time and concentration of Al-ion on the structural properties of ZnO thin

films. The study reported a diminishing intensity of (002) upon Al-doping. That is increasing the concentration of Al-ions over a long aging time reduces the intensity of the peak. And also, the aging time had a random effect on crystalline size of the size.

Jellal et al., [32] investigated the microstructural and optoelectronic properties of AZO films deposited by fine-channel mist chemical vapor deposition (FCM-CVD) technique. The authors considered four different Al-concentration such as 5%, 10%, 25% and 50%. From the structural characterizations, the researchers remarked that for dopant concentration below 25%, the peak (002) was the most dominant, which indicates that the preferential orientation of the growth of the AZO film at lower Al doping is along the c-axis. However, it was observed that increasing the doping concentration of the Al content leads to a drastic change of preferential orientation from (002) c-axis to (100) a-axis direction.

From figure 2, it can be observed that at higher Al doping concentration, the diffraction peak (002) seemingly disappeared, while the peak (100) becomes strongly dorminant. This result shows that the excessive presence of Al ions in the ZnO matrix favors the growth of the films along a-axis. That is the films are vertically aligned in one direction forming nanorods. This implies that the nanorods of ZnO thin films can be achieved just by increassing the amount of Al-ions present in the ZnO matrix.

Rersearch has shown that nanorod thin films are excellent materials for optioelectric applications. Therefore the films with 50% Al-ions possess better crystal quality for optoelectronic apllications. However, it has been experimentally agreed that the diffraction peak along c-axis (002) is the peak that determine the crystallinity of the films; then it could be implied that excessive addition of aluminum content into the matrix of the ZnO films has capacity of distorting the crystal quality of the film as previouly indicated that larger incorporation of aluminum elements induces stress and could lead to diminshing of the crystal quality of the film.

Furthermore, the alteration in the preference orientation occasioned by the large additon of the Al could be due to the stress/strain caused by the ionic size mismatch between aluminum and zinc [33].

However, beyond ionic size mismatch, there are other factors that could create stress in the films such as the impurities, defects, and lattice distortion in the crystals, or lattice mismatch and thermal expansion coefficient mismatch between the film and substrate. The stres/strain induced by the aformentioned factors causes a broadness in the diffraction peaks which in turn leads to the reduction of grain size of the film.

Generally, the FWHM of film is very sensisitive to stress and it is inversely related to the grain size of the film. Moreover, recently, researchers have opined that the extrinsic stress can be overlooked or negligible if the films thickness is large enough to maintain grain boundary stability [33-35].

The stress in a film can be classified based on the stress value, if the stress value is positive, the films are said to be in tensile states for which the optical band gap of the films is expected to decrease, but if the stress value is negative then the films are in compressive state where the optical band gap increases. Therefore, stress in the films can be an important parameter for determining the optoelectronic properties of the films.

In essence, for AZO film to be suitable for optoelectronic application, the amount of stress in the film has to be as low as possible, and to achieve this feat, the deposition process must be monitored to minimize the occurance of impurities, and using substrate that matches lattice quality of the film.

ZnO thin films doped with Al-dopant concentration ranging from 0 to 10% is considered to be in tensile state, and the transmittance of the films was oberved to decrease with increasing Al-dopant concentration from 0 to 10%, this effect was attributed to the increase in the charge density which resulted in a higher absorption of the photon reaching the films [36].

Perhaps, for higher concentrations of the dopant like 25% and 50%, the transmittance increased and this could be due to an increase in the number of void in the films according the SEM result shown in figure 3.

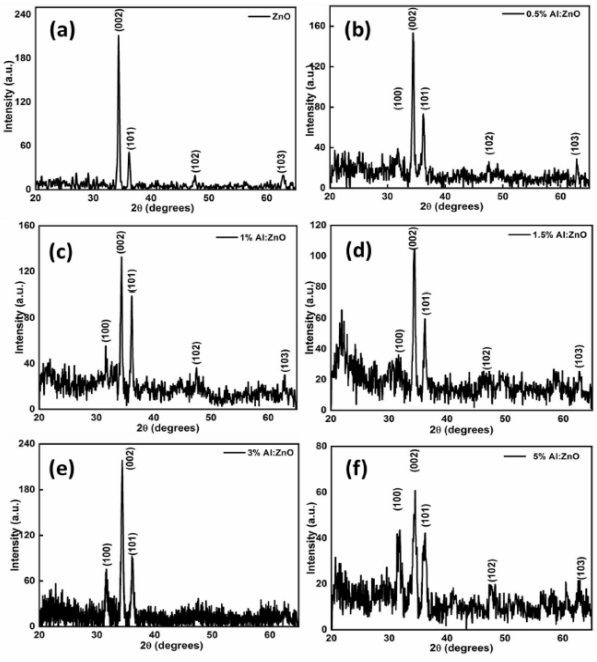

Figure 2: XRD spectra of undoped and doped ZnO thin film with different Aluminium concentrations [41]

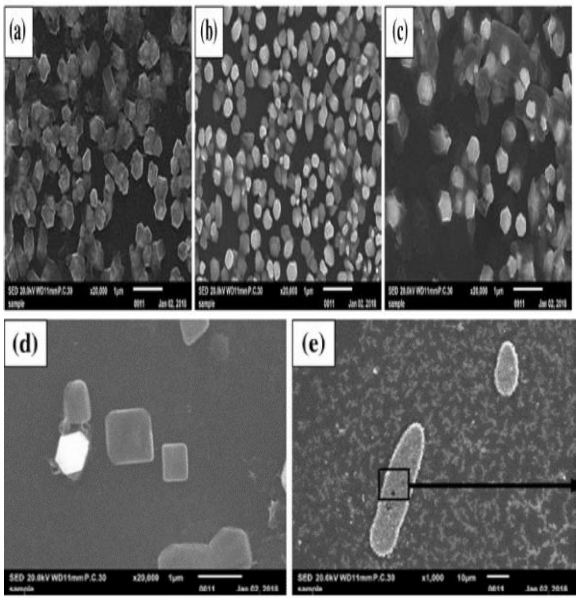

Figure 3: SEM image of undoped and doped ZnO thin films, a) undoped, b) 5% Al doping, c) 10% Al doping, d) 25% Al doping, and e) 50% Al doping [36]

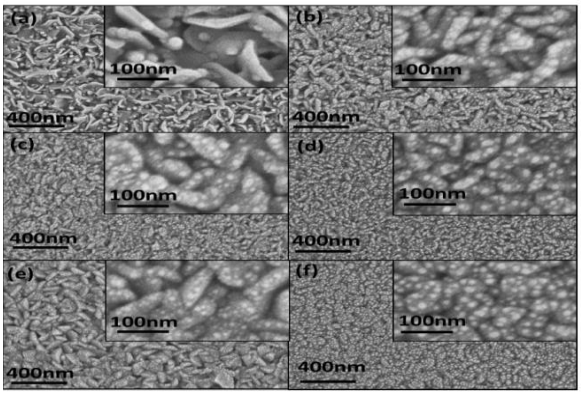

Figure 4: SEM image of pure and Al-doped ZnO thin film, a) 0 at%, b) 0.5 at%, c) 1 at%, d) 1.5 at%, e) 3 at%, and f) 5 at% [41]

The SEM images of the surface of the layers are shown in figure 3, the SEM image of the pristine and 5% doped ZnO showed that the films' surfaces reveal no structural surface defects, their morphologies indicate a homogenous arrangment of fabricated samples. However, it was observed that the structural quality got affected upon increasing dopant concentration to 10%, 25%, and 50%. The increase in the content of the Al dopant in the matrix of ZnO created more pores or space in between the grains causing a change in the grain formations and morphological view of the thin film.

However, from figure 4, it can be observed that lower Al-doping concentration from 0.5% to 5% for the AZO thin films, a uniform distribution of granular morphological structure without the presence of pores or cracks was observed. The pristine ZnO thin film possess a randomly packed nano-plate like structure. More so, upon the introduction of Al-ions the morphological structure of the pure ZnO films transformes from plate-like structure into granular morphology.

Effects of concentration of Al-dopant, aging and annealing on the properties of AZO films have also been studied extensively [37]. The researchers focused their work primarily on the influence of the aging time, concentration of Zn, and annealing temperature on the structural properties of Al-doped ZnO thin films. The AZO films were fabricated on a glass substrate using spin coating followed by annealing. The XRD results confirm that the films had a decrease in grain size with aging time up to 72 hours for low Zn concentration of 0.2 M and 0.4 M, for high concentration of 0.6 M and 0.8 M, the grain size increased only up to 48 hours.

However, it was understood that increasing aging time had a significant effect on the grain size which is a remarkable tool to evaluate the resistivity of the films, since decrease in the grain size below certain threshold point has potential disadvantage of increasing the resistance of the film. The largest grain sizes were obtained at Zn concentration of 0.4 M at 72 hours and 0.6 M at 48 hours.

Kathwate et al. [38] synthesized Al-doepd ZnO thin films by chemical pyrolysis technique. The structural study of the research is ncentred on the crystal quality and the morphological characteristics of the Al-doped ZnO in respect to the Al-doping concentrations. The result of the X-ray diffraction patterns indicate that all the Al-doped ZnO thin films are polycrystalline in nature and matches well with the hexagonal (wurzite) ZnO crystal structure; which implies that the presence of any secondary phase in the samples was not detected after doping with Al ions, and no changes in the hexagonal crystal structure within the Al-doping concentrations.

However, the Al-doping had a sigtnificant effect on the intensity of the diffraction peaks of the samples; it was observed that increasing the concentration of the Al doping enhance the intensity of the peak (002) along the c-axis direction.

This result also supports the previous reports that at lower Al-doping content, especially below 5% Al, the growth of the Al-doped ZnO is always along the c-axis. It implies that the crystallinity of the AZO thin films depends largely on the amount of the Al-ions present in the matrix of the ZnO thin film. The results obtained in the study are in good agreement with precious studies [39].

Lee and coworkers [40] had also reported preferred crystal growth of Al-doped ZnO along the c-aixs (002). Kathwate and coworkers reported that the stress in the Al-doped ZnO increases with increasing Al-doping concentrations; it can be seen from figure 5 that the stress increrases monotounsly as the Al-doping. However, the strain in the AZO thin films decreases with increasing Al-doping concentration. The stress and strain in the AZO thin films is an indication of presence of defects and impurity contents which causes a broadness in the

diffraction peaks leading to a decrease in the particle or grain size of the thin film as shown in figure 2.

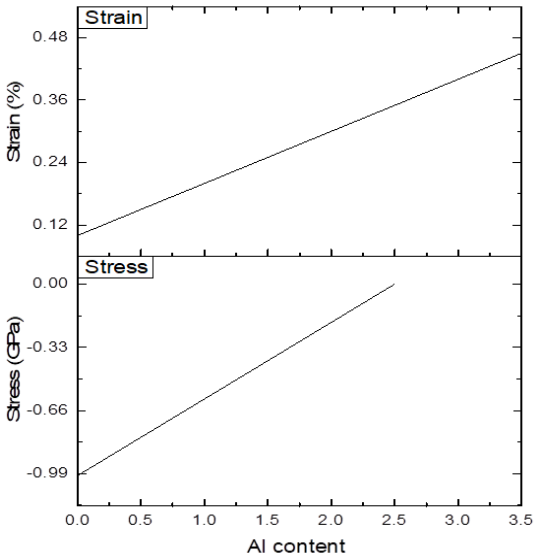

Figure 5: A graph of strain and stress for Al-doped ZnO thin films with different Al-doping concentration [38]

However, the nature of the morphology of the AZO thin films as revealed by the FE-SEM, showed a cluster of spherical nanoparticles with an particles size of about 25 nm and decreases to 19 nm after Al-doping. The reduction in the particle could be as a result of the shrinking of ZnO lattice due to doping with small sized Al-atoms. The reason behind the reduction in the partilce size can also be supported by the variation in the intensity of the diffraction peaks in the XRD patterns. Similar observations had been noted previously [41]. The Al-doping transformed the ZnO nanoparticles into nanosheet-like structure.

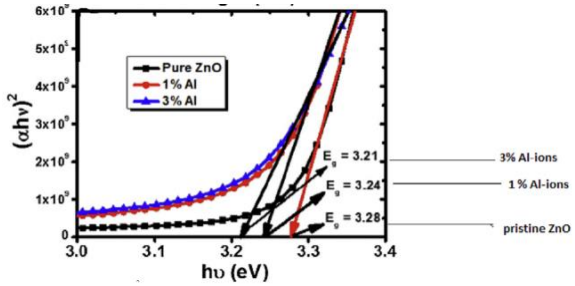

Figure 6: Tauc plot of (ahv)2 against hv, showing the optical band gap for pristine and Al-doped ZnO

The optical properties of the Al-doped ZnO thin films are exploited for optoelectronic applications; knowing how the incorporation of the Al-ions into ZnO influences the optical properties of ZnO will provide an understanding of the suitability of the material in device appllication in the area of solar cells, optoelectronic and as a transparent electrode.

Many researches have been carried out on the optical properties of Al-doped ZnO thin films; many of these studies reported improvement on the optical properties especially the optical band gap energy of the material upon Al-doping. However, Al-doped ZnO thin films have exhibited good optical transmittance in the visible regions, but upon high Al-doping concentration, the transmittance started to decrease. This decrease is as a result of the variations in the grain size and surface morphology of the AZO thin films.

The optical band gap energy was noted to decreases from 3.28 eV to 3.21 eV for ZnO samples doped with 1% to 3% Al-dopant. This means that the presence of the Al-ions in the ZnO the decreases the resistance of the the valence electrons from migrating into the conduction band by making them more energtic and improving the optical conduction of the AZO thin films [38].

Figure 6 shows the Tauc plot of $(\alpha h\nu)^2$ against hv for pristine and Al-doped ZnO with two different concentrations such as 1% and 3%. The plot reveals that the optical band gap of the AZO films was decreases upon increasing Al-doping concentrations.

In another study on the optical properties of the Al-doped ZnO thin films, Jellal and his coworkers [32] investigated the influence of Al-doping concentration on the optical band gap of ZnO thin films. The authors considered four different concentrations such as 5%, 10%, 25%, and 50%.

The results of the study showed that the transmittance reduced with increasing Al-doping content from 0 to 10%, this reduction in the transmittance could be as a result of the increase in the charge density which causes a large absorption of photons approaching the samples.

However, at higher Al-doping concentration, the optical transmittance was observed to increase trememdously as the result of the formationn of more pores or void in the surface of the Al-doped ZnO thin films. This is correct due to the previously reported study which had suggested that large Al-doping creates some intrinsic defects such as point defect in the form of voids or pore or even grain boudary which act as sites for absorption.

Furthermore, the optical band gap increases with increasing Al-doping concenterations. Increase in the absorption would correspondingly increase the transmitting power of the film surface. The value of the band gap were recorded to be 3.3 eV, 3.21 eV, 3.25 eV, 3.88 eV, and 3.86 eV for Al-doping concentrations of 0%, 5%, 10%, 25%, and 50%.

The result indicates that at lower Al-doping content such as 5% and 10%, the optical band gap decreases upon Al-doping relatively to the pristine ZnO; more so, the optical band gap began to increase when the Al-doping content exceeds the 10%. The increase in the optical band gap with increasing Al-doping could be as a result of the formation of interstital Al_2O_3 compound in the ZnO phase.

The same result had previously been reported where the optical band gap increased from 3.23 to 3.73 eV after doping with Al-

ions as the content increases from 0 to 24.6 at% respectively [39].

The electronic band structure of thin films controls the optical band gaps of the material. understanding how the Al-doping affects the electronic structrure gives an ideal on the relationship between the band gap and Al-doping. It has been reported that the presence of Al ions in the ZnO matrix causes a shift of the Fermi level towards the conduction band, resulting in a deep donor level in the conduction band; this characteristic enhances the performance of the material as an n-type semiconductors [40].

The optical properties such as the transmittance and optical band gap are important parameters that are strongly considered during device fabrications and optoelectronic applications. Bharath [41] investigated the effect of Al-doping on the optical transmission and bandgap of ZnO thin films. The author carried out the optical measurements in the wavelength range of 350 – 700 nm. The study reported about 95% transmittance for ZnO film doped with 1.5 at% and 3 at%.

Moreover, it was reported that the optical transmittance decreased to 80% upon increasing Al-doping. The decrease in the transmittance of the Al-doped ZnO could be attributed to reduction in the crystallinity of the films as shown in the decrease of intensity and increase in broadness of (002) peak. The reduction in the crystal quality can be believed to have caused a scasttering in the material due to the large surface roughness in the film.

The graph of transmittance agaianst wavelenght is shown in figure 7a with respect to the Al-doping concentrations. The Al-doping had little or no effects on the optical band gap of the films as seen in figure 7b; the linearlity noted in the Tauc's graph is an indication that the sample is n-type semiconductor. The estimated band gap is in the range of 3.27 eV for all films.

Fucheng and coworkers had reported on the effect of Al-doping on the defect behaviors of ZnO thin films as a photocatalyst. On the optical examination, the authors reported a random increase in the optical band gap with increasing Al-doping concentration. The evaluation was done on 0.3 at%, 1 at%, 1.5 at%, and 2 at% Al-doping concentrations, the corresponding band gaps are 3.249, 3.25, 3.256, and 3.253 eV respectively [42].

Sarma et al. [43] investigated the influence of pulsing frequency on the optoelectronic properties of AZO films fabricated on quartz substrate by pulsed DC magnetron sputtering. The AZO films were produced at sputtering power of 80 W with pulsing frequencies in the range of 50 – 100 kHz. The structural results indicate that the AZO films with best crystal quality were obtained at a pulsing frequency of 75 kHz.

More so, at the same pulsing frequency the AZO films demonstrated excellent visible light transparency and limited transparency in the naer-infrared region due to free carrier absorption. The sheet resistance of the AZO films at 75 kHz pulsing frequency was observed in the range of 9 – 45 Ohm/sq. This characteristic however makes AZO deposited at 75 kHz pulsing frequency suitable for optoelectronic applications. The figure of merit as high as $1.99 \times 10^{-2}\Omega^{-1}$ was achieved at that pulsing frequency.

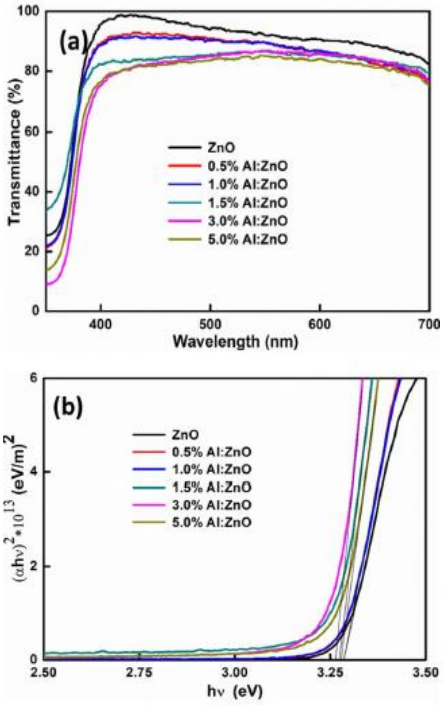

Figure 7: Optical plots of (a)Transmittance spectra, (b) Tauc's plot of pure and Al-doped ZnO with various Al concentrations

The high figure of merit and strong thermal stability in the ambient oxidizing environment exhibited by the sputtered AZO films fulfill the requirement for transparent electrode in solar cell applications. This result has elucidated the fact that deposition method plays a vital key in the properties of thin films.

Summarily, it has been established that the Al-doping has a significant effect on the crystal quality and morphological properties of the Al-doped ZnO thin films. However, it was understood that at larger Al-doping concentration especially from 50% Al and above, the diffraction peak of (002) disappears and the peak of (100) became very dense.

Further, at the Al-doping within the content of 1% to 25%, the diffraction peak of (002) is the most dominant peak. The number of pore and space in the morphology of the films also increased upon increasing the concentration of the Al-ions in the matrix of ZnO thin films.

Al-doping was observed not to have significant effect on the optical transmittance of the AZO thin films; however, it was noted that at larger Al-doping the transmittance increases due to the increase in the number of pores or void created by the high Al-doping concentration.

The optical band gap energy was hugely affected by the Al-doping, it was revealed that at high Al-doping content, such as beyond 5 at%, the optical band gap increases so rapidly, more than that of pristine ZnO thin film. Therefore, it can be asserted that to obtain a high-quality Al-doped ZnO thin films that can be suitable for optoelectronic devices application, such films have to be doped with Al-ion less or equal to 5 at%.

The Al-doped ZnO with 5 at% Al-ions have shown to exhibit high uniform morphology with little or no pores or void. However, in the cases where the Al-doped ZnO films are desired for gas sensing application, porous morphology is the more wanted; in this case, doping with more than 5 at% Al ions is highly recommended.

3 Effect of Al-dopant on the electrical properties of Aluminum-doped ZnO (AZO) thin film

The recent advances made on the Al-doped ZnO in relation to its application s in optoelectronic devices are discussed here. The primary aim of the present review work is on the influence of the Al-dopant on the electrical conductivity spanning from carrier mobility, carrier concentration and electrical resistivity.

Hjiri et al., [44] fabricated Al-doped ZnO using a modified sol-gel technique for highly sensitive CO gas sensors; the AZO films were annealed at 400$^{\circ C}$ after fabrication for proper dehydration. The researchers analyzed the electrical characteristics of AZO films using a four-point contact method. They reported that the incorporation of aluminum into the ZnO films remarkably improved the electrical conductivity of the film. Moreover, there was a strong decrease in the electrical resistance after the addition of 1% Al; as the Al concentration increases, the electrical resistance continues to decrease, although to a lesser extent.

Again, the authors also argued that the sensors based on Al-doped ZnO exhibited a higher response than the pure ZnO samples. It is necessary to note that, at high doping concentration, the disorder produced in the lattice increases the efficiency of the scattering mechanisms, such as phonon scattering and ionized impurity scattering which has the potential to increase the resistivity of the films [45]; this phenomenon leads to the accumulation of space charge potential barriers across the grain boundaries [46]. This is because excessive Al-doping could result to a dramatic decrease in the grain size and a sufficient space charge region can be developed.

Furthermore, due to the low resistance of the core region of the grain boundary and the high resistance of the space charge region, the resistance in the AZO thin films seems to increase with decreasing grain size after the grain size exceeds a certain value. Therefore, while increasing the Al-doping in ZnO matrix to improve the electrical properties of the films, caution must be exercised not to over dope the film.

A graph of resistance against Al-doping is shown in figure 8. It can be seen from the graph that the resistance of the AZO thin film decreases continuously with increasing Al-doping concentrations suggesting an improvement in the electrical conductivity, since decrease in electrical resistance results in an increase in conductivity.

This result shows that at larger Al-doping concentrations, the AZO thin film might reach a point of zero resistance; that is a point of superconductivity could be achieved upon doping ZnO with large amount of Al ions.

From figure 8, it is imperative to note that the resistance of the AZO thin films approaches zero value towards Al-doping content of 5% and above.

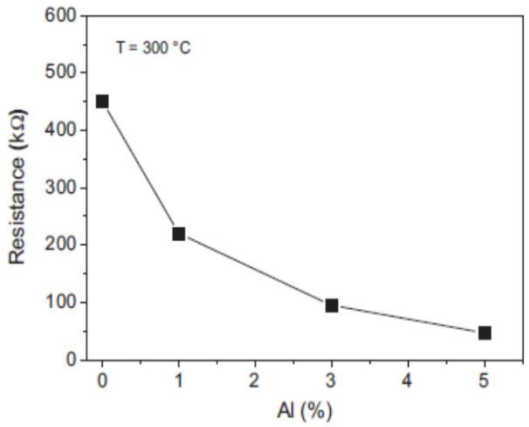

Figure 8: A graph of electrical resistance against Al-content [46]

Bangera et al. [41] investigated the electronic and gas sensing properties of Al-doped ZnO thin films. The authors fabricated the AZO films by simple spray pyrolysis technique using Zinc diacetatedihydrate and Aluminum chloride as the precursor materials and dopant material respectively. The study considered five Al-doping concentrations, such as 0.5 at%, 1.0 at%, 1.5 at%, 3.0 at%, and 5 at%.

From the results of electrical measurement; the resistivity of the samples decreases linearly with increasing aluminum doping concentration, a minimum resistivity of 0.517 Ohms was achieved at 3% Al-doping content. This result is slightly in disagreement with the previous study where the minimum resistivity was achieved at 6% [46]. The difference in the result could be due to the method of film fabrication.

Al-Ghamdi et al. [47] fabricated AZO thin films using spin coating technique. The author reported that the charge carrier mobility, concentration, and electrical conductivity all increased with increasing the concentration of Al-doping. In a similar way, Dominic Potter et al., [48] had reported high conductivity, carrier concentration and low resistivity at 10 at% Al-doping.

Cheng et al. [49] reported low resistivity of $1.08 \times 10^{-3}\ \Omega cm$ at 4% Al-doping content. However, Y. Khaaissa et al. [50] studied the influence of 2 at%, 4 at% and 8 at% Al-doping

content on the optical and electronic properties of AZO thin films fabricated by spray pyrolysis on glass substrate.

From the hall-effect measurement, the authors reported highest carrier concentration of 1.2×10^{20} cm with 2.3 cm^2/Vs mobility and lowest resistivity of 2.7×10^{-2} Ωcm for the 4 at% Al-doped ZnO thin film.

Ji et al., [51] evaluated the effect of substrate temperature on the electrical properties of Al-doped ZnO fabricated on glass substrate by RF magnetron sputtering technique. The study showed that the temperature of the substrate had a significant influence on the electrical characteristics of the AZO thin films. It was observed from the electrical characterization that at substrate temperature of 320℃ the AZO thin films showed best electrical properties with a resistivity of 3.53×10^{-4} Ωcm , carrier mobility of 39.33 cm^2/V and carrier concentration of 4.50×10^{20} cm^{-3}.

Islam et al., [52] studied the effect of Al-doping on electrical properties of Al-doped ZnO thin film deposited by sol-gel method. The study measures the electrical properties of pure and Al-doped ZnO thin films using Van der Pauw four-point collinear probe method. The resistivity was calculated using the following formula $\rho = 2\pi s\,(V/I)$, where V is the potential difference between the inner probes in volts, I is current flowing through the outer pair of probes in ampere, S is the spacing between the probes in meter. The pure ZnO had higher electrical resistivity which decreases rapidly upon the introduction of Al-doping; and continues to decrease progressively with increasing the Al-doping concentration into the lattice sites of ZnO thin films.

However, due to the excellent electrical and optical properties exhibited by Al-doped ZnO thin films, the material has recently been employed to design transparent heaters; these transparent thin film heaters are applied in cleaning automobile windows, mirrors, and outdoor displays under extreme environmental condition. Thin film heaters have demonstrated capacity to replace the hydrophobic coatings for anti-icing (to prevent the formation of ice) applications because of the poor mechanical and chemical stability of the hydrophobic coatings in severe weather conditions [53].

The emerging applications of thin film heaters are essentially for wearable body heater and for personalized heating [54]. Transparent window has been proposed to be key component for next generation energy efficient building; however, for thin films to be considered excellent transparent heater, such thin films are expected to exhibit low sheet resistance, high thermal stability and high transmittance. For decades now, indium thin films have been widely used as transparent thin film heater due to their excellent optical properties, high conductivity (10 Ohm/sq.); however, due to its low thermal response and failure to perform in certain applications that require flexibility has limited its usage. On the other hand, Al-doped ZnO thin films have shown to perform better in this condition than the ITO.

Upon this regard, Jayathilake et al. [55] fabricated Al-doped ZnO thin films onto a glass substrate by aero assisted chemical transport (AACT) and evaluated the film's application as transparent thin film heater. The authors reported a sheet resistance of 142.5 Ohm/sq. for AZO films at a thickness of 400 nm, which corresponds to a resistivity of 5.7×10^{-3} Ωcm. The most important property of a thin film heater is the sheet resistance of the material, the lower the value, the better its power efficiency.

To measure the thermal stability of the AZO film, the author measured the power consumption of AZO film over input voltage 6, 9, 12, 15 and 18 V using a thermal image camera. The films were allowed to heat for 10 min and then cool back to room temperature. The power consumption was recorded to be 0.267, 0.578, 0.950, 1.56 and 2.11 W for applied voltage of 6, 9, 12, 15, and 18 V respectively.

Furthermore, Jayathilake and coworkers examined the thermal of AZO thin films heaters by switching the applied voltage from 0 to 18 V for 18 cycles; a voltage of 18V was applied for 5 min, followed by 0 V for 5 min. An average temperature of 130℃ was attained when 18V was applied for 5 min. It was observed that the sheet resistance remained constant despite the variations in temperatures; that is before and after the stability test, this result suggests that the AZO thin films heater is stable for rapid variations in temperature for a long period of time without possible degradation.

The results obtained from the thermal measurement confirms that the AZO thin film can be used as an alternative material to indium tin oxide (ITO) for transparent thin film heater application. It is important to assert at this point that the thermal properties of the thin film heater are largely dependent on the electrical and thermal conductivity and specific heat capacity of the active material and the heating performance ultimately depends on the substrate condition.

Kurtaran [56] fabricated Al-doped ZnO thin films by spray pyrolysis technique and examined the influence of different annealing time on the electrical properties of the films. The prepared AZO thin films were annealed in the MSE furnace (1200℃) at 400℃ in an air medium for 1.5, 3, and 6h and the films were allowed to cool down to room temperature in the annealing furnace; the films were nicknamed as ZA1, ZA2, and ZA3 according to annealing time respectively. The electrical characterizatiuon was done by four-point probe method.

The results show that the AZO thin film annealed for 3h had the least electrical resistivity of 1.39×10^{1} Ωcm, invaribaly having better electrical properties; the AZO films annealed for 6h had the largest electrical resistivity of 5.02×10^{1}Ωcm and the AZO film annealed at 1.5h had the moderate resistivity of 2.44×10^{1} Ωcm. The least resistivity observed in ZA2 was due to the formation of oxygen vacancies created during the annealing process, the open annealing favors the creation of oxygen vacancies within the short time of 3h, however, when the thermal agitation continues beyond 3h, the oxygen vacancies began to be filled with oxygen atoms which forms a restriction in the path of charge carriers leading to reduction in

the mobility of the carrier and in turns increases the resisitivity of the films.

It has been noted experimentally that annealing in an air medium increases the formation of oxygen atoms and reduces the creation of oxyegen vacancies; when there is low number of oxygen vacancies in the surface of the film, the mobility of the cariier would be reduced by scattering at the grain boundary resulting in a larger electrical resistivity of the AZO film as seen in ZA3. That is to say, increasing the annealing time of the AZO thin films in the air medium favours the formation of oxygen molecules, which promotes the formation of oxygen interstitials and suppressing the creation of vacancies. The oxygen vacancies are known to be a pathway for the motional movement of free electrons in the material [57]. This result has indicated that a controlled annealing time influences significantly the electrical properties of AZO thin films.

The plot of resisitivity versus annealing time is shown in figure 9. From the plot, it can be seen that the resistivity decreases from 2.44 to 1.39 Ωcm with increase in annealing time from 1.5 to 3h and increases rapidly to 5.02 Ωcm as the annealing time increases to 6h. that is, the resistivity increases progressively with increase in annealing time from 3h above.

Zhang et al. [58] investigated the influence of ZnO cap layer morphology on nthe electrical properties and thermal stability of Al-doped ZnO film. The authors focussed their evaluations on the influence of substrate temperature and and annealing in air and Ar on the electrical properties of Al-doped ZnO thin films. The ZnO cap layers were fabricated by chemical vapor deposition onto Al-doped ZnO (AZO) thin films; the AZO thin films were prepared by magnetron sputtering on glass substrate at various substrate temperatures such as 550, 600, and 650℃.

The electrical characterization was done by four-point probe method; the results of the study show that the ZnO cap layers exhibited a reduction in the electrical resistivity of the AZO thin films; however, after deposition at a substrate temperature of 600℃, a continuous formation of ZnO cap was achieved which leads to an enhancement in the Hall mobility from 22 to 37 $cm^2V^{-1}S^{-1}$, resulting in a resistivity of 5.1×10^{-4} Ω cm which was observed to be higher than those of nanoparticles and nanorods morphologies formed at lower and higher substrate temperatures, respectively.

It was also noted that the continuous ZnO cap layers sufficiently stop a decrease in the carrier concentration and Hall mobility during annealing at the temperature of up 600℃ in air. Furthermore, annealing the capped AZO films in air at 600℃ reduced the carrier concentration and the Hall mobility moderately to 1.2×10^{-20} cm^{-3} and 30 $cm^2V^{-1}S^{-1}$ respectively; this causes an increment in the resistivity of the films to 1.7×10^{-3} Ωcm and figure of merit de creased to 1.6×10^{-1} Ω^{-1}. The improvement of the electrical properties of the AZO thin films was due to the cap layers providing proper morphology to sufficiently protect the grain boundary by reducing the defect that might have been a trapping site to charge carriers.

Kumar and coworkers studied the effect of seed-layer thickness on the electrical conductivity and carrier mobility of sputtered grown Al-doped ZnO thin films [59]. The study indicates that the AZO thin films deposited on the ZnO seed layer had well improved electrical properties than the AZO thin films deposited without the ZnO seed layer. The Hall mobility, electrical resistivity and carrier concentration of AZO thin films without seed layer were measured to be 8.19 ± 0.06 cm^2/Vs, $(2.70 \pm 0.04) \times 10^{-3}$ Ω cm, and $(2.82 \pm 0.02) \times 10^{20}$ cm^{-3} respectively. When the AZO thin films were fabricated over the ZnO seed layer the electrical properties were excellently enhanced. The Hall mobility, resistivity and carrier concentration of AZO thin films increased to 15.21 ± 0.04 cm^2/Vs, $(5.54 \pm 0.03) \times 10^{-4}$ Ω cm, and $(7.42 \pm 0.02) \times 10^{20}$ cm^{-3}, respectively.

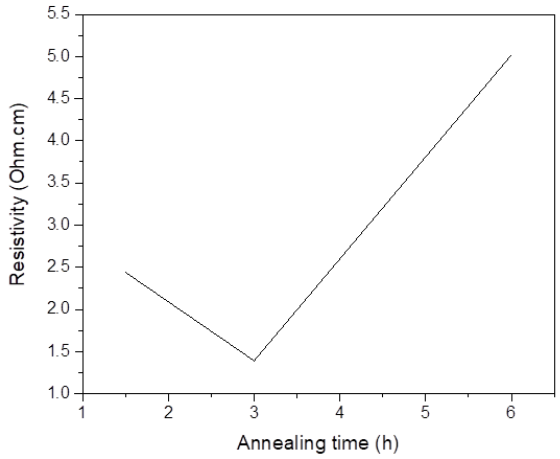

Figure 9: A plot of resistivity versus annealing time for Al-doped ZnO thin films

More so, the electrical conductivity of the AZO thin films prepared with the seed layer was found to increase by five-fold and reach a maximum value of 1806.94 ± 10.5 S/cm, which is also greater than the average value required for any transparent conductive oxide material for optoelectronic applications. The enhancement of the electrical conductivity of AZO thin film over seed layer can be attributed to improvement in Hall mobility and carrier concentration of the AZO films.

The high optical transmittance of the AZO films can also be attributed to the large carrier density of AZO deposited with seed layer. The free electrons can be seen to occupy the bottom state of conduction band which could increase the energy gap of available optical transition level from the valence band top to bottom of conduction band leading to an increase in optical band gap energy of the AZO film with seed layer. The electrical conductivity and optical transmittance of thin films are the two main parameters that are considered for figure of merit (FOM) of transparent conductive oxide materials.

The figure of merit (FOM) of thin films is a factor that determines the suitability of the film to be used as a high performing TCO. A high value of figure of merit means better

quality of TCO thin film. The figure of merit of AZO was calculated by the formula:

$$\frac{T^{10}}{R_S} \quad (1)$$

where T and R_s are the transmittance and sheet resistance of the thin film.

The calculated FOM are $2.72 \times 10^{-3}\ \Omega^{-1}$ and $1.68 \times 10^{-2}\ \Omega^{-1}$ for AZO thin film deposited without seed layer and with seed layer respectively. The seed layer assisted AZO thin films showed FOM higher than that without a seed layer; this result obtained here is better than previously reported FOM on AZO thin film and TCO/metal/TCO structure.

The plot of Hall mobility, carrier density, and electrical resistivity are shown in figure 10. From the plots, it can be seen that the Hall mobility and carrier density of the AZO thin films deposited with seed layer tripled compared with that without the seed layer; also, the electrical resistivity of the AZO films with the seed layer decreased significantly compared the AZO films without seed layer.

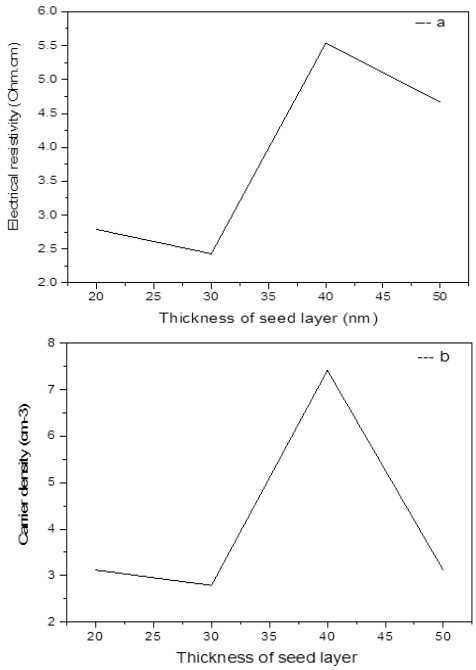

Figure 10: Plot of (a) electrical resistivity and (b) carrier density against seed layer thickness

The electrical resistivity and carrier density of AZO thin films increase progressively with the thickness of ZnO seed layer from 20 to 40 and decrease from 40 to 50 nm. The plot of thickness of seed layer versus the electrical resistivity, and carrier density are shown in figure 11a, b. The result therefore shows that the ZnO seed layer plays a remarkable role in the improvement of the electrical properties of the AZO thin films.

Kumar & Ahmad [70] studied the role of defects and microstructure on the electrical properties of solution processed Al-doped ZnO transparent conducting films. The authors focus their evaluations on the influence of Al-doping concentrations on the mobility, carreir concentrationa and electrical resisitivity of AZO thin films. The electrical measurement was done using the Hall-effect measuring systemby Van der Pauw method. The results show that the resisitivity reduced, while the carrier density increases with increasing Al-doping content up to 2 at%. However, when the Al-doping was increased to 3 at%, the carrier concentration was observed to decrease and the electrical resistivity increased rapidly.

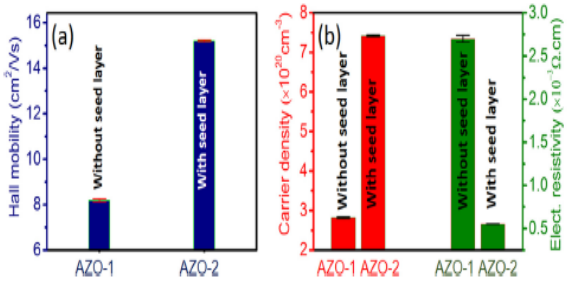

Figure 11: Hall mobility and (b) carrier concentration and electrical resistivity of AZO thin films deposited without (AZO-1) with (AZO-2) seed layer [59]

It has been experimentally confirmed that the electrical resistivtiy decreseas with increasing charge carrier density and Hall mobility; also mit has been reported that maximing charge density above the order of 10^{21} cm^{-3} leads to a reduction in the Hall mobiliy [71].

Therefore it can be asserted that the lowest electrical resistivity of 1.2×10^{-2} Ωcm and maximum electrical conductivity of 83.33 S/cm were achieved at 2 at% Al-doping concentration. Further more it was observed doping the ZnO thin film with 3 at% and above had adeteriorating effect on the electrical quality of the AZO, therefore the best Al-doping is found to be 2 at% . Devi and coworkers [72] studied the the electrical properties of 3 at% and 6 at% Al-doped ZnO thin films; and reported incresase in the electrical resistivity with Al-doping concentration. However, in comparison with the pristine ZnO, the Al-doped ZnO had a better electrical quality. The study recorded electrical resistivity of 0.006499 and 0.0005749 Ohm.cm for 3% and 6% Al doping content respectively.

The summary of electrical resistivity and conductvity is shown in table 1. However, the influence of substrate on the optical and electronic properties of Al-doped ZnO thin films has been investigated [73]. The authors prepared AZO thin films on ITO glass substrate and polyyethylene teterephthalate (PET) substrate using atomic layer deposition (ALD). The fabricated AZO thin films on both substrates exhibited high optical transmittance at visible and near-infrared spectra regions and improved electrical properties. notwithstanding, the AZO films deposited on the PET substrate demonstrated stable sheet resistance over 1000 bending cycles than that on the ITO glass substrate.

The study recorded changes in the thickness of the films; it was 100 nm for AZO/PET and 206 nm for AZO/glass. Further

more, the AZO films deposietd on the ITO glass substrate exhibited better electrical properties than that on the PET substrate, this result is furher supported by the high thickness observed in the AZO thin films synthesized on the glass substrate which may have pavced ways for the formation of oxyegen vacancies in the AZO/glass leading to an increrase in the Hall mobility in the film. It is well established that increase in Hall mobility means decreases in electrical resistivity and improved conductivity of the films.

Figure 12 shows the plots of curent versus applied for AZO films deposited on glass and PETsubstrates; though both plots obey Ohm's law but the sheet resistance of the AZO films on glass substrate was lowerr than that on the PET substrate indicating better electrical properties.

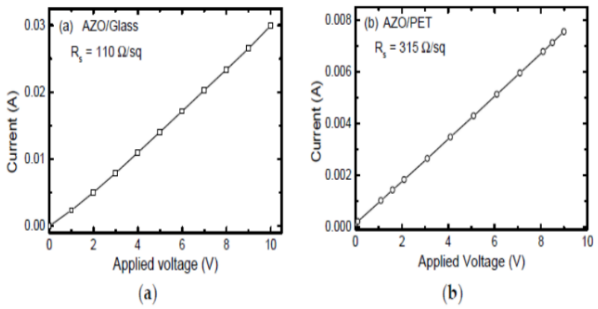

Figure 12: A plots of current-voltage relationship for AZO/Glass and AZO/PET [73]

Ghosh et al. [73] fabricated ZnO thin films reinforced with Al-dopant to improve the electrical conductivity for applications in perovskite solar cells. The authors tried to reduce the deteriorating effect of Al doping of ZnO on its optical and crystallinity by adopting an annealing process using Zn blanket. They understood that doping ZnO film with any dopant has the capacity of negatively influencing the intrinsic properties of films, however, doping would enhance the electrical properties but the crystallinity and optical properties could be sacrificed.

The authors focused on striking a balance between high electrical properties and quality crystal quality. The AZO films were deposited by RF sputtering in a chamber at a fixed pressure of 25 mTorr with an RF power of 150 W. A post thermal treatment of the fabricated AZO film was carried out at 550℃ with Zn films for 1hr in Ar^+ 10% H_2 ambient.

During the heat treatment, the Zn and AZO film were kept in blanket style so that the Zn film remains in close proximity to the AZO film. The AZO film of fixed thickness of 200 nm was annealed with Zn film of various thicknesses such as 20 nm, 40 nm, and 80 nm, also, AZO film of various thickness of 200 nm, 350 nm, and 500 nm were annealed with Zn films with fixed thickness of 80 nm.

The authors focused their evaluations on the influence of the heat treatment on the properties of the AZO films with respect to the Zn films as a blanket. It was observed from the structural results that the AZO films" roughness, crystallite size increases with increasing Zn thickness after the annealing process, moreover, the intensity of (002) peak was found to decrease with an increase in the Zn thickness during annealing in blanket style.

The optical examination revealed a high transparency of 85-95% in the visible range for all the films. However, a change in the optical transmission was noticed with an increase in the thickness of Zn and AZO films and the value is approximately more than 90% in the visible region for AZO 350 nm thickness with 80 nm Zn thickness and greater than 85% for AZO 500 thickness with 80 nm Zn thicknesses.

These transmission values are comparable with the commercially available ITO with thickness 180 nm. This result indicates that AZO of thickness 350 nm and 500 nm with 8 nm Zn can conveniently replace ITO as a transparent conductive oxide in solar calls and optoelectronic devices. The authors recorded the lowest resistivity of 3.1×10^{-4} Ω cm with figure of merit value of 6.5×10^{-2} Ω-1 for RF sputtered 350 nm AZO thin film.

The low sheet resistance was attributed to a decrease in the number of defects and increase in Hall mobility in the AZO films. Further, the authors applied the developed AZO film as a conducting substrate to fabricate perovskite solar cells and it was proven that the AZO film as a conducting substrate significantly improved the electrical properties and energy conversion efficiency of the perovskite solar cells.

In summary, it has been shown sufficiently that the presence of Al-dopant in the matrix of ZnO thin films significantly enhances the electrical conductivity and reduces resistivity of the film. However, it has been observed that increasing the Al-doping concentration beyond a certain value such as 5 at%, does not increase the electrical quality of the film rather increases the resistivity and minimizes electrical conductivity.

It is evidently noted that doping ZnO with 5% Al and above increases the resistivity of the film, but doping with 3% Al or lower significantly improves the electrical properties of the AZO thin films.

4 Effect of Al-dopant on the gas sensing properties of Al-doped ZnO thin films

The Al-doped ZnO thin films have demonstrated strong gas sensing properties that are employed in sensing applications for gasous molecules. Hazardous abd health threatening gaseous molecules in our environment has continued to degrade the safety of human lives and that of animals.

Making the environemnt clean and green has dominated the focus of recent researches nowadays. However, developing gas sensors that can significantly detect the malicious gaseous molecules will profoundly improve the safety of the environment and save lives. Unfortunately, most of the well known gas sensors operate at high temperature; this is because the gases are not reactive to sensing materals at room temperature.

Furthermore, the high-temperature operation of these sensing devices increases power consumption which causes frequenct battery replacement; thereby increasing the cost of operation and limits the life span of the sensors. Therefore developing gas sensing materials that operate at room temperature and capable of detecting the leakage of these hazardous gases is a necessity. Moreover, several kinds of gas sensor that operate at room temperature have been fabricated based on transition metal dichalcogenides (TMDs), graphene and carbon nanotubes (CNTs) [74-77).

Cho and coworkers [78] investigated the room temperature sensing properties of an atomic layer of MoS_2 to NO_2, and reported a strong affinity of MoS_2 to the gas.

Jeong et al. [79] prepared CNT/reduced graphene hybrid films exhibiting room temperature NO_2 gas sensing properties attributed to the high specific area of the hybrid composite film.

Further, Yuan et al. prepared chemically moidified graphene and demonstrated its room temperature sensitivty to NO_2 gas, which was attributed to its high carrier mobility abd large specific surface area [80]. However, upon all the breakthrough recorded in the development of these gas sensing devices, their practical applications are limited by some fundamental issues.

Kim and coworkers [81] reported some of the limitations associated with TMD-based gas sensors to be poor gas selectivity, short lifetime, sluggish recocvery characteristics and diffuculty in the fabrication of large scale devices.

Zaporotskova et al. [82] reported that CNT-based gas sensors demonstrtae high sensitivity but require a long exposure time, yet its irreversible change in conductivity, lack of selectivity and inability to identify gases with low adsorption energies has limited its practical application.

On the hand, Verghese et al., reported some disadvantages of grephene gas sensors in terms of their sensitivity, detection limit abd repeatability [83]. However, even though these above mentioned gas sensors demonstrate room temperature selectivity, yet their responses have been very unreliable with incomplete recovery time. Hence, these gas sensors are not suitable for practical application.

Interestingly, Zinc oxide based chemiresistive gas sensors are fascinating devices that have shown capacity to overcome these known limitations due to their high response to various gases, low cost of fabrication, and long life time [84].

Sharnkar and Rayappan have recently fabricated ZnO nanorods with flat, sharp pencil-type, and burnt-end morphologies. The authors reported room temperature sensitivity of the deposited ZnO thin film to ethanol [85]; additionally, Zhang and coworkers reported the room temperature sensing properties of prepared dendritic ZnO nanostructures to H_2S [86].

However, it is important to submit that the mechanism of the room temperature sensing properties of these films are not clearly explained and the authors literally attributed the characteristics to the complicated, fascinating and unusual nanostructure, therefore further study is thoroughly needed to understand the room temperature selectivity and sensitivity of these ZnO based gas sensors.

Sanger and coworkers [87] investigated the room temperature gas sensitivity of morphology controlled free-standing hollow aluminum doped Zinc oxide (AZO) nanofibre for NO_2 gas sensor. The authors fabricated the free standing hollow nanofibres using a polyvinylpyrrolidone fibre template electrospun on a copper electrode frame followed by radio-frequency sputtering of an AZO thin overlayer and heat treated at 400℃ to burn off the polymer template.

The results of the research revealed that the gas sensors based on the hollow nanofibres exhibited full recoverable n-tyep room temperature sensing ability of low concentration of NO_2 (0.5 ppm); whereas the gas sensors built with Al_2O_3 filled AZO nanofibres demonstated no gas sensitivity below 75℃.

The gas sensitivity of the sensors was determined by the density of molecules above the minimum energy for adsorption, collision frequency of gas molecules with the surface, and available adsorption sites. The adsorption sites are promoted by porous morphology; that is, increase in the porosity of the film, the better the ability of the films to adsorb the gaseous molecules on the surface.

Furthermore, the authors reported that the gas sensing with fully recoverable and room temoperature sensitivity of the free standing hollow AZO fibres toward 0.5 ppmn NO_2 gas was due to the high collision frequency of NO_2 molecules inside the hollow core and its high surface to volume ratio. This method described here by the researchers is perhaps an improved way of realizing the room temperature sensitive sensors with one dimensional nanostructure.

In a similar way, Kolhe et al. [88] fabricated Al doped ZnO thin films by using simple chemcial spray pyrolysis technique and investigated the gas sensing performance for H_2S detections. The sensing characterisitic of the undoped and Al-doped ZnO thin films were estimated by varying the resistance of the thin film in the presence and absence of H_2S gas in the temperature range of 100 – 300℃.

The sensor response of the undoped and Al-doped ZnO films was measured for a fixed concentration of H_2S (600 ppm) and the corresponding results indicated that, the Al-doping significantly improved the sensing properties. Again, at 200℃ with 600 ppm H_2S gas, the response of the AZO films doped with 0.002 M of Al was found to be three-times that of undoped ZnO sensors, and it is six-times that of undoped ZnO for 0.004 M of Al-dopant.

The exposure of the film to H_2S gas caused a decrease in the resistance of the films; this can be attributed to increase in carrier concentration due to adsorption of H_2S gaseous molecules on the surface of the films. Moreover, it was observed that at low exposure temperature such as 100℃ and 150℃, the response of the AZO sensor was low due to low

activation of thermal energy on the surface of AZO films which limited response of the H_2S gas.

This result indicates that the activation energy is very necessary for the detection of H_2S gases and the highest sensor response was noted at temperature of 200℃. Above this temperature, the responsiveness of the AZO sensor was observed to decrease rapidly for the temperature 250℃ and 300℃. At this high temperature, the H_2S gas kept reacting with the oxygen adsorbed on the surface of the sensor instead of reacting with the films as expected; this behavior caused a reduction in response.

Kathwate et al., [89] fabricated Al-doepd ZnO thin films b y chemical pyrolysis technique; the authors focused their evaulation on the gas (ammonia) sensing properties. The ammonia gas sensing properties of the AZO films were evaluated at 25 ppm concentration of ammonia gas in air at 100℃ operating temeprature.

The meaurement showed that upon exposure of both pure and Al-doped ZnO film to NH3 gas, a remarkable decrease in the electrical resistance of the ZnO sensing layer was observed. The reason for this observation could be due to the oxidizing nature of the ammonia gas. However, it was noted that the response and recovery time of Al-doped ZnO film is significantly low compared to undoped ZnO film.

Moreover, it was observed that the gas sensitivity of the AZO sensor to ammonia gas increases upon increasing Al doping concentration. The authors remarked that the increase in the gas sensing properties of Al-doped ZnO films might be due to the structural and morphological variations that occcurred as a result of the introduction of the aluminum element into the ZnO matrix. The decrease in the average grain size of the films led an increase in the sensor's sensitivity performance. The result showed that the Al-doped ZnO sensors exhibit good response for ammonia gas at temperature of 100℃ and low gas concentration of 25 ppm.

Generally, it has been experimentally reported that the gas sensing properties of oxide materials largely depend on the material's morphology and changes in resistance due to adsorption of target gas molecules [90]. The comparison of the gas sensing properties of pristine and Al-doped ZnO thin film sensors as reported by various authors is shown in table 2 for undoped and Al-doped ZnO film sensor as reported by various authors.

Chaitra and coworkers [91] fabricated both undoped and Al doped zinc oxide thin film for the detection of low concentration of sulphur dioxide gas (SO2). The researchers deposited the ZnO films by sol-gel spin coating technique. The authors focused on the attention on the SO_2 gas sensing properties. The study considered four Al-doping concentrations, such as 1 at%, 2 at%, 4 at% and 6 at%.

The wrinkled morpholgy reported in the study was found to improve the gas sensing properties of the sensor; this is because the wrinkled kind of morphology allows the high adsorption of gaseous molecules on the surface of he film, by promoting direct interactuion between the gasous moelecules and the film. The maximum gas sensitivity of 71% for 3 ppm of SO_2 at 300℃, which is found to be below the threshold level value (5 ppm) was achieved for a Al-doping concentration of 2 at%. The study indicated that at higher Al-doping content, the sensitivity of the sensor was decreased.

Kundu et al. [92] synthesized aluminum doped zinc oxide (AZO) thin films on sodalime glass subtrates by using jet-atomizer spray pyrolysis technique. The precursor solution was a mixture of zinc nitrate hexahydrate and aluminum nitrate monohydrate at five different Al doping concentrations 0 at %, 1 at %, 3 at % and 5 at%. The fabricatd AZO films were calcined at various temperature ranging from 450 to 650℃ in steps of 50℃.

The authors focused their evaluatuions on improving the humidity sensing prioperties of Al-doped ZnO films. The study reported that the porous morphology of the AZO film aided the improvement of the sensing properties of the film. It was understood that increasing the Al-doping concentration significantly increased the number of pores or holes in the AZO thin films.

However, the nanoporous structured Al-doepd ZnO thin films was reported to have played a remarkable role in the agglomeration and nattachment of foreign particles on the surface of the films; thus making the film suitable for gas sensing application owing to its capacity of adsorption of gas molecules on the surface of the AZO film. This result in a large extent validated the importance of film morpholoty on the gas sensing application.

The humidity sensing properties such as responsivity, sensitivity, repeatability, response time and recovery time of the Al-doped ZnO films were examined at room temperature in the range of 10 to 90% relative humidity (RH). A gradual increase inn the responsivity of AZO films was observed below 70% RH, howeevr, beyond this level, a rapid increase in the responsivity with increasing Al-doping concentration was obviously noted.

This rise in the responsisvity with Al-doping content with chnages in relative humidity indicates an increase in the resistance of the AZO upon adsorption of molecules of water. This is because adsorption of foreign particles such water or other gaseous elemts on the surface of the AZO has the tendecy of eliminating the possible oxygen vacancies leading tom a reduction to the Hall mobility of trhe AZO films.

The saturated solutions of NaOH, CH_3COOK, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, were employed to achieve the stable relative humidity level as 10, 20, 22, 37,53, 70, 80, 90 % respectively. At 5 at % of Al doping concentration, the AZO thin films exhibited the highest reponsivity of 733% at 90% relative humidity.

Generally, the responsivity of any thin film is dependent on the film sporosity, this is because the sample porosity creates more

active sites in the material, and the more the active sites in the film, the greater the adsorption of foreign particles including gas molecules on the surface of the films.

The porous morphology is shown in figure 13; and it can be seen that the number of surface pores increases with increasing Al-doping content.

Likewise, the sensitivty of AZO was found to increases with increase in Al doping concentration, however, the undoped ZnO showed no changes in its sensitivity throughout the operating range of relative humidity whereras the AZO thin films doped with 3 at % of Al exhibited the largest/strongest sensitivity.

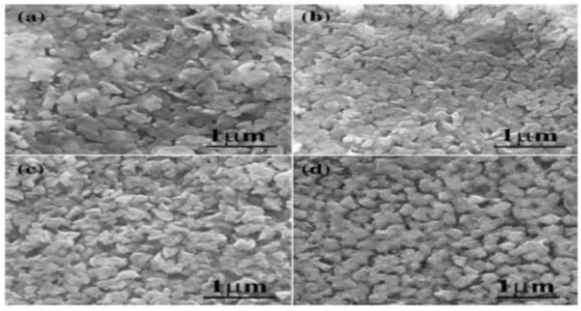

Figure 13: FE-SEM morphoplogy of a) 0 at%, b) 1 at%, c) 3 at%, and d) 5 at% [92]

Table 1: Electrical resistivity and conductivity of Al-doped ZnO thin films

Method of deposition	%at Al-dopant/condition	Resistivity (Ohm.cm)	Electrical conductivity (S/cm)	Figure of merit (FOM)(Ω−1)	Reference
Spray pyrolysis	Annealed for 3hr	1.39×10^{1}	7.19		[56]
	10 at% Al	1.08×10^{-3}	925.93		[49]
Spray pyrolysis	4 at% Al	2.7×10^{-2}	37.03		[50]
RF magnetron sputtering	Substrate temp. 350℃	3.53×10^{-4}	2832.86		[51]
Magnetron sputtering	Annealed at 600℃	1.7×10^{-3}	588.23		[58]
Sputtering	AZO	5.53×10^{-4}	1806.94	1.68×10^{-2}	[59]
Sol-gel	AZO	4.27×10^{-1}	2.34	6.27×10^{-8}	[60]
Sputtering	AZO	7.14×10^{-4}	1400.56		[61]
Sputtering	AZO	3.49×10^{-3}	286.45		[62]
Sputtering	AZO	6.68×10^{-4}	1497.00		[63]
Chemical vapor deposition	AZO	8.68×10^{-4}	1152.07		[64]
Chemical vapor deposition	AZO	9.9×10^{-3}	101.01		[65]
Sputtering	AZO	2.8×10^{-2}	35.76		[66]
ALD	AZO	1.2×10^{-3}	833.33		[67]
Sputtering	AZO	1.0×10^{-3}	1000.00		[68]
Sputtering	AZO	1.2×10^{-3}	833.33		[69]
Chemical	2 at% Al	1.2×10^{-2}	83.33		[70]
PLD	3 at% Al	4.2×10^{-3}	233.97		[72]

Table 2: Comparison of gas sensing properties of undoped and Al doped ZnO film sensors as reported by various authors

Materials	Deposition method	Morphology	Target gas	Gas response and optical temperature	Reference
Undoped ZnO thin films	Spray pyrolysis	Nano-crystalline	NO_2 and H_2S	7 ppm & 100℃	91
Undoped ZnO thin films	Microwave assited	Flower	CO	200ppm & 300℃	92
AZO thin films	Spray pyrolysis	Nanoflakes	H_2S	600 ppm & 200℃	88
AZO thin films	Spray pyrolysis	Hexagonal	H_2S	200-100 ppm & 200℃	77
AZO thin films	Spray pyrolysis	Hexagonal	Methanol	500 ppm & 275℃	94
AZO thin films	Simple chemical method	Spherical nanoparticles	NO_x	20 ppm & 100℃	95
AZO thin films	Sol-gel	Nanorods	Ammonia	100 ppm & 350℃	86
AZO thin films	Chemical bath deposition	Nanowires	NO_2	10 ppm & RT	96
AZO thin films	Hydrothermal method	Hierarchial narcissus	NO_2	1 ppm & 240℃	85
Pt-AZO films	Hydrothermal method	Spherical	Acetone	10 ppm at 450℃	86
AZO thin films	Sol-gel spin coating	Wrinkle like structure	SO^2	3 ppm at 300℃	91
AZO thin films	Chemical bath method	Nanorods	NO_2	100 ppm at 350℃ 50 ppm, 100 ppm	100
AZO thin films	Spray pyrolysis	Celuster structure	Ammonia		99

The mechanism of humidity sensing of AZO thin film is presented in figure 14. The lowest sensitivity value of 0.07 MΩ/RH% was obtained for 5 at% AZO films at 90% relative humidity. The sensing mechanism of the AZO thin films reported here can be employed to explain the water adsorption technique and possibly make a strong prediction about the cause of increase in resistance of the AZO sensors during water adsorption.

Handan Aydin et al. [93] synthesized Al-doped ZnO thin films on a microscopic slide substrate at five different Al dopant concentrations (0.1 %, 0.5%, 1%, 2%, and 5%) by sol-gel spin coating technique. The study examined the ammonia gaas sensing properties. In order to evaluate the gas sensing properties of the AZO film, the changes in the electrical resistance was measured over the presence of the gas molecule on the surface of the films at room temperature using ammonia gas.

The AZO sensors were exposed to ammonia gas at different rates 660 ppm, 1000 ppm, and 1330 ppm. The response values calculated for AZO sensors were dependent on the grain size of the AZO film, and the responsivity of the films increases with decreasing grain size. This is because the smaller the gain size the higher the poroity in the film, (that is increase in gap in the films) which increases the active sites for adsorption of the gas molecules, thus enhancing the gas detection ability.

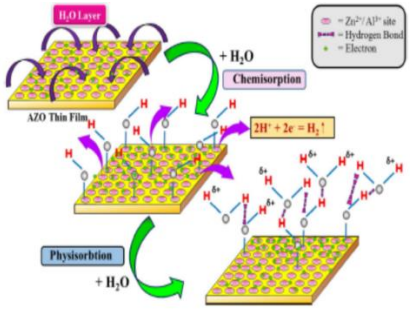

Figure 14: Schematic presentation of humidity sensing mechanism of AZO thin films [92]

The highest response of the AZO films was observed at Al doping concentration of 5% same concentration with the highest roughness. It shows that the responsivity of the fims is directly proportional to the roughness in the films. Moreover, since the amount of gas moleucles in the film increased as the roughness value increases, then the gas detection ability of the AZO films also increased.

This result has further shown that the AZO thin films exhibiting these properties can be utilized in clinical diagnosis, health industry, environemntal protection and cooling sytems in order to determine the leaks of ammonia gas in high toxic level. Namgung and coworkers [94] studied the gas sensing properties of diffusion driven Al-doped ZnO nanorods. The AZO nanorods were deposited on Si substrate by chemical bath deposition. The authors examined the gas sensing capability of the AZO nanorods by exposing the nano-film to the NO_2.

It was observed that the AZO nanorods had a significant reponse of 120.4% at 350℃ to 100 ppm of NO_2 gas. However, surprisingly a relatively sharp response was retained even at room temperature, although the recovery speeds were somehow slowed down. Moreover, the responses of AZO nanorods to 50 and 100 ppm of NO_2 at room temperature were calculated to be 4.2 and 10.5% respectively.

The authors deposited stretchable AZO based sensors on a PDMS substrtae employing both bilayers of AZO NRs and AgNWs. The Ag nanowires were used to reduce the sensors resistance and facilitate the gas reactivity of AZO NRs. The fabricated stretchable AZO based sensors were able to detect about 10 ppm of NO_2 gas at room temperature under 30% strain. It was observed that the response under a large strain of 30% was rather large than the response at zero strain.

The sensing mechanim as proposed by the authors could be used to explain the oberved room temperature and strain state NO_2 gas sensing performance. The incorporation of aluminum dopants into the matrix of ZnO thin films have proven to significantly reinforce the electrical conductivity and gas sensing properties of AZO thin films.

These gas sensors developed using aluminum doped ZnO thin films can also be used to improve the sensitivity and selectivity and other properties of some artificial intelligent devices to detect the presence of harmful gases in the environment, this will help to make a prompt alert to consumers, enhance medical diagnosis and improve the quality of our living standards.

A flexible and stable pH sensor based on aluminum-doped zinc oxide nanosheets (AZO NSs) has been fabricated by a low cost hydrothermal technique. The results obtained from the study indicated that Al ions successfully doped into the matrix of ZnO nanostructure could influence the morphology and improve the pH sensing properties.

The pH sensitivity of Al-doped ZnO nanosheet of 50.2 mV/PH with a correlation coefficient of around 0.99468 was obtained; and when compared with that of pure ZnO film (34.13 Mv/PH) ZnO nanowires (45.89 Mv/PH), an improvement in the sensitivity of AZO was noted. The test range of pH values were broadened by Al-doping and the AZO nanosheet sensors was observed to detect the pH value ranging from 2 to 12.

It was remarkably observed that in a more acidic environment basically for a pH value of 2, the Al-doped nanosheet sensors were strongly stable over a period of 12 weeks of testing, and the response time was completely fast and the response time of the sensors for each pH standard buffer solution was around 0.3 second.

It is remarkably important to submit that based on the excellent pH sensing properties manifested by the Al-doped nanosheets, such high sensitivity, good long term usage, good flexible property, and the use of small amount of test liquid, the nanosheets can be employed in medical diagnosis and treatments especially for the detection of pH value of cancer patient which will monitor the chemcial environment of their body systems [95].

Besides ZnO based metal oxide semiconductor, many studies have been reported on numerous pH sensors based on metal oxide such as Tin (IV) oxide (SnO_2), Tungsten trioxide (WO_3), and Titanium dioxide (TiO_2). However, ZnO based pH sensors have demonstrated an improved efficiency than other metal oxide semiconductors due to its excellent properties including high exciton binding energy (60 meV) at room temperature, high band gap, just to mention a few.

In summary, it is proven substantially that the Al-dopant enhances the gas sensing properties of the ZnO thin films. However, it was recorded that the porous morphology created by the presence of the Al-ion in the ZnO significantly aided the im provement of the gas sensing properties.

This is because, the pores and hole act as active site for the adsorption of the gaseous molecules and other foreign particles on the film's surface. Increase in the concentration of the Al-doping increases the sensitivity of the Al-doped ZnO sensor but decreases the responsivity of the sensor. The best gas sensing properties were obtianed at 5 at% Al-doping conentration.

5 Conclusion

The electrcal properties and gas sensing properties of zinc oxide thin film are some of the most important properties that have been extensively exploited in the fabrication of optoelectronic devices and gas sensors. Reinforcing these properites using conductive metal elements has become a benchmark for the continuous manufacturing of miniaturized ZnO based electronic devices.

This review evaluated the structural, optical electrical properties and gas sensing properties of zinc oxide (ZnO) films doped using aluminum ions. The study substantially showed that the incoporation of aluminuim ions into the lattice of zinc oxide (ZnO) thin films significantly enhanced the electrical conductivity and gas sensing properties of the Al doped ZnO films.

The presence of aluminum ions in the ZnO thin films was found to create appreciable number of pores or voids in the films, which are observed to be active sites for the adsorption of foreign particles especially gas molecules. This porous morphology of the Al-doped ZnO film was noted to be a key factor in making the AZO films suitable for gas sensing applications. However, It was adequately understoond that increasing the Al doping concentration in ZnO films beyond 6% deteriorated the crystallinity, reduced the grain size and created stress/strain in the film.

This development further increased the optical scattering and subsequently reduced the optical tranmittance of the films. Therefore an extensive effort must be made to ensure that the crystallinity of the Al doped ZnO films does not deteriorate while improving the electrical quality and gas sensing properties.

On this basis, we recommend adopting Taguchi optimization statistical method to evaluate the effect of Al concentration, and other deposition parameters on the overall properties of ZnO thin films before the proper fabrication. This mechanism will invaribly control the nature of the AZO film deposited.

Also employing electrodeposition route will also support to mitigate the influence of Al content on the structural quality of the film; because electrodeposition has proven to be an efficient route for fabricating large area textured transparent electrodes at low cost with superb structural quality.

Acknowledgements

The authors appreciate the nano-technology laboratory, Tshwane University of Technology, Pretoria, South Africa for providing access to internet.

Declaration of Competing Interest

The authors declare no conflict of interest in the funding of this work.

References

[1] Y. F. Hu, Y. L. Chang, P. Fei, R. L. Snyder, and Z. L. Wang, “Designing the electric transport characteristics of ZnO micro/- nanowire devices by coupling piezoelectric and photoexcitation Effects,” ACS Nano, vol. 4, no. 2, pp. 1234–1240, 2010

[2] Z. R. Tian, J. A. Voigt, J. Liu et al., “Complex and oriented ZnO nanostructures,” Nature Materials, vol. 2, no. 12, pp. 821–826, 2003

[3] L. Gong, J. G. Lu, and Z. Z. Ye, “Transparent conductive Ga- doped ZnO/Cu multilayers prepared on polymer substrates at room temperature,” Solar Energy Materials & Solar Cells, vol. 95, no. 7, pp. 1826–1830, 2011

[4] Z. L. Wang and J. H. Song, “Piezoelectric nanogenerators based on zinc oxide nanowire arrays,” Science, vol. 312, no. 5771, pp. 242–246, 2006

[5] D. Tamvakos, S. Lepadatu, V. A. Antohe et al., “Piezoelectric properties of template-free electrochemically grown ZnO nanorod arrays,” Applied Surface Science, vol. 356, pp. 1214– 1220, 2015.

[6] P. S. Shewale and Y. S. Yu, “Structural, surface morphological and UV photodetection properties of pulsed laser deposited Mg-doped ZnO nanorods: effect of growth time,” Journal of Alloys and Compounds, vol. 654, no. 5, pp. 79–86, 2016

[7] J. J. Li, L. T. Zhang, J. B. Zhu, Y. Liu, and W. C. Hao, “Aligned ZnO:Co nanorod arrays: Electrophoretic deposition fabrica- tion and magnetic manipulation,” Ceramics International, vol. 41, no. 3, pp. 3456–3460, 2015.

[8] S.K. Mishra, D. Kumari, B.D. Gupta, Surface plasmon resonance based fiber optic ammonia gas sensor using ITO and polyaniline, Sens. Actuators B 171–172 (2012) 976–983

[9] M. Sinha, R. Mahapatra, B. Mondal, T. Maruyama, R. Ghosh, Ultrafast and reversible gas-sensing properties of ZnO nanowire arrays grown by hydrothermal technique, J. Phys. Chem. C. 120 (2016) 3019–3025

[10] M. Sundararajan, P. Sakthivel, A.C. Fernandez, Structural, optical and electrical properties of ZnO-ZnS nanocomposites prepared by simple hydrothermal method, J. Alloys Compd. 768 (2018) 553–562

[11] A. Franco Jr., H.V.S. Pessoni, Enhanced dielectric constant of Co-doped ZnO nano particulate powders, Physica B 476 (2015) 12–18.

[12] S. Singh, P. Dey, J.N. Roy, S.K. Mandal, Tunable dielectric constant with transition metal doping in Zn1-x(MnTM)xO (TM ¼ Co, Fe) nanocrystals, J. Alloys Compd. 642 (2015) 15–21.

[13] Bizarro, M. High photocatalytic activity of ZnO and ZnO: Al nanostructured films deposited by spray pyrolysis. Appl. Catal., B 2010, 97 (1), 198−203.

[14] Saravanakumar, K.; Sakthivel, B.; Ravichandran, K. Simulta- neous doping of aluminum and fluorine on zinc oxide nanopowder using a low-cost soft chemical route. Mater. Lett. 2011, 65 (14), 2278− 2280

[15] M. Jiang, X. Liu, H. Wang, Conductive and transparent Bi-doped ZnO thin films prepared by rf magnetron sputtering, Surface & Coatings Technology, 203 (2009) 3750- 53

[16] Y. Ammaih, A. Lfakir, B. Hartiti, A. Ridah, P. Thevenin, and M. Siadat, ‘Structural , optical and electrical properties of ZnO : Al thin films for optoelectronic applications’, pp. 229–234, 2014, doi: 10.1007/s11082-013-9757-2.

[17] N. Srinatha, P. Raghu, H. M. Mahesh, and B. Angadi, 'Spin-coated Al-doped ZnO thin films for optical applications : Structural, micro-structural, optical and luminescence studies', *J. Alloys Compd.*, vol. 722, pp. 888–895, 2017, doi: 10.1016/j.jallcom.2017.06.182.

[18] Berginski, M.; Hupkes, J.; Schulte, M.; Schope, G.; Stiebig, H.; Rech, B.; Wuttig, M. The effect of front ZnO:Al surface texture and optical transparency on efficient light trapping in silicon thin-film solar cells. J. Appl. Phys.2007, 101, 074903.

[19] Minami, T.; Sato, H.; Nanto, H.; Takata, S. Heat treatment in hydrogen gas and plasma for transparent conducting oxide films such as ZnO, SnO2 and indium tin oxide. Thin Solid Films 1989, 176, 277–282

[20] Dhere, R.G.; Bonnet-Eymard, M.; Charlet, E.; Peter, E.; Duenow, J.N.; Li, J.V.; Kuciauskas, D.; Gessert, T.A. CdTe solar cell with industrial Al:ZnO on soda-lime glass. Thin Solid Films 2011, 519, 7142–7145

[21] Vasekar, P.S.; Dhere, N.G.; Moutinho, H. Development of CIGS2 solar cells with lower absorber thickness. Sol. Energy 2009, 83, 1566–1570

[22] Park, S.; Ikegami, T.; Ebihara, K. Growth of transparent conductive Al-doped ZnO thin films and device applications. Jpn. J. Appl. Phys. 2006, 45, 8453–8456

[23] Saravanakumar, B.; Mohan, R.; Thiyagarajan, K.; Kim, S. J. Investigation of UV photoresponse property of Al, N co-doped ZnO film. J. Alloys Compd. 2013, 580 (15), 538−543

[24] Verma, A.; Khan, F.; Kumar, D.; Kar, M.; Chakravarty, B.C.; Singh, S.N.; Husain, M. Sol–gel derived aluminum doped zinc oxide for application as anti-reflection coating in terrestrial silicon solar cells. Thin Solid Films 2010, 518, 2649–2653.

[25] Mondragon-Suarez, H.; Maldonado, A.; de la L Olvera, M.; Reyes, A.; Castanedo-Perez, R.; Torres-Delgado, G.; Asomoza, R. ZnO:Al thin films obtained by chemical spray: Effect of the Al concentration. Appl. Surf. Sci. 2002, 193, 52–59.

[26] Ma, J.; Ji, F.; Ma, H.; Li, S. Preparation and properties of transparent conducting zinc oxide and aluminium-doped zinc oxide films prepared by evaporating method. Sol. Energy Mater. Sol. Cells 2000, 60, 341–348

[27] Liu, Y.; Lian, J. Optical and electrical properties of aluminum doped ZnO thin films grown by pulsed laser deposition. Appl. Surf. Sci. 2007, 253, 3727–3730

[28] Yang, W.; Wu, Z.; Liu, Z.; Pang, A.; Tu, Y.; Feng, Z.C. Room temperature deposition of Al-doped ZnO films on quartz substrates by radio-frequency magnetron sputtering and effects of thermal annealing. Thin Solid Films 2010, 519, 31–36

[29] Tynell, T.; Yamauchi, H.; Karppinen, M.; Okazaki, R.; Terasaki, I. Atomic layer deposition of Al-doped ZnO thin films. J. Vac. Sci. Technol. A 2013, 31, A109-A1–01A109-4

[30] C. H. Lee and D. W. Kim, 'Preparation of Al doped ZnO thin films by MOCVD using ultrasonic atomization', pp. 12–16, 2014, doi: 10.1007/s10832-014-9895-3.

[31] D. T. Speaks, 'Effect of concentration , aging , and annealing on sol gel ZnO and Al-doped ZnO thin films', 2020.

[32] Y. Hou, A.M. Soleimanpour, A.H. Jayatissa, Low resistive aluminum doped nanocrystalline zinc oxide for reducing gas sensor application via sol–gel process, Sens. Actuators B 177 (2013) 761–769

[33] L. Cao, L.P. Zhu, J. Jiang, R. Zhao, Z.Z. Ye, B.H. Zhao, Highly transparent and conducting fluorine-doped ZnO thin films prepared by pulsed laser deposition, Sol. Energy Mater. Sol. Cells 95 (2011) 894–898

[34] Dimitrov, Dimitre, Che-liang Tsai, Stefan Petrov, Vera Marinova, Dimitrina Petrova, Blagovest Napoleonov, and others, 'Atomic Layer-Deposited Al-Doped ZnO Thin Films for Display Applications', 2020, 1–12, doi: 10.3390/coatings10060539

[35] E. Manikandan, V. Murugan, G. Kavitha, P. Babu, and M. Maaza, 'Nano flower rod wire-like structures of dual metal (Al and Cr) doped ZnO thin fi lms : Structural , optical and electronic properties', *Mater. Lett.*, vol. 131, pp. 225–228, 2014, doi: 10.1016/j.matlet.2014.06.008.

[36] A. A. Al-Ghamdi, O. A. Al-Hartony, M. El Okr, A. M. Nawar, S. El-Gazzar, Farid El-Tantawy, F. Yakuphanoglu, Spectrochemic Acta Part A; Molecular Biomolecular Spectroscopy, 131, 15 October 2014, 512-517

[37] D. T. Speaks, 'Effect of concentration , aging , and annealing on sol gel ZnO and Al-doped ZnO thin films', 2020

[38] Kathwate, L. H., Umadevi, G., Kulal, P. M., Nagaraju, P., Dubal, D. P., Nanjundan, A. K., & Mote, V. D. (2020). Ammonia gas sensing properties of Al doped ZnO thin films. Sensors and Actuators, A: Physical, 313, 112193. https://doi.org/10.1016/j.sna.2020.112193

[39] P. Banerjee, W.-J. Lee, K.-R. Bae, S.B. Lee, G.W. Rubloff, J. Appl. Phys. 108, 043504 (2010)

[40] H. Ahmoum, M. Boughrara, M.S. Su'ait, M. Kerouad, Chem. Phys. Lett. 719, 45 (2019)

[41] S. P. B. K. V Bangera, 'Fast detection and discriminative analysis of volatile organic compounds using Al - doped ZnO thin films', *Appl. Phys. A*, pp. 1–10, 2021, doi: 10.1007/s00339-021-04771-8.

[42] X. Zhang, Y. Chen, S. Zhang, and C. Qiu, 'High photocatalytic performance of high concentration Al-

doped ZnO nanoparticles', *Sep. Purif. Technol.*, vol. 172, pp. 236–241, 2017, doi: 10.1016/j.seppur.2016.08.016

[43] B. Sarma, D. Barman, and B. K. Sarma, 'Applied Surface Science AZO (Al : ZnO) thin films with high figure of merit as stable indium free transparent conducting oxide', vol. 479, no. January, pp. 786–795, 2019, doi: 10.1016/j.apsusc.2019.02.146.

[44] M. Hjiri, L. El Mir, S. G. Leonardi, A. Pistone, L. Mavilia, and G. Neri, 'Sensors and Actuators B : Chemical Al-doped ZnO for highly sensitive CO gas sensors', *Sensors Actuators B. Chem.*, vol. 196, pp. 413–420, 2014, doi: 10.1016/j.snb.2014.01.068

[45] M. A. Kaid and A. Ashour, Applied Surface Science. Volume 253, Issue 6, 15 January 2007, Pages 3029-3033

[46] E. Manikandan, V. Murugan, G. Kavitha, P. Babu, and M. Maaza, „Nano flower rod wire-like structures of dual metal (Al and Cr) doped ZnO thin films : Structural , optical and electronic properties", Mater. Lett., vol. 131, pp. 225–228, 2014, doi: 10.1016/j.matlet.2014.06.008

[47] A. A. Al-Ghamdi, O. A. Al-Hartony, M. El Okr, A. M. Nawar, S. El-Gazzar, Farid El-Tantawy, F. Yakuphanoglu, Spectrochemic Acta Part A; Molecular Biomolecular Spectroscopy, 131, 15 October 2014, 512-517

[48] Dominic B. Potter, Davinder S. Bhachu, Michael J. Powell, Jawwad A. Darr, Ivan P. Parkin,and Claire J. Carmalt, Phys. Status Solidi A 213,No. 5, 1346–1352 (2016)

[49] K. Cheng *et al.*, Applied Surface Science Surface microstructure evolution of highly transparent and conductive Al-doped ZnO thin films and its application in CIGS solar cells", *Appl. Surf. Sci.*, vol. 409, pp. 124–131, 2017, doi: 10.1016/j.apsusc.2017.03.044

[50] Y. Khaaissa et al., (2020) Ultrasonic Spray-Assisted CVD Growth of Highly Transparent and Conductive Aluminum-doped ZnO, Surface Review and Letters, doi: 10.1142/S0218625X20500249

[51] Ji, X., Song, J., Wu, T., Tian, Y., Han, B., Liu, X., Wang, H., Gui, Y., Ding, Y., & Wang, Y. (2019). Solar Energy Materials and Solar Cells Fabrication of high-performance F and Al co-doped ZnO transparent conductive films for use in perovskite solar cells. *Solar Energy Materials and Solar Cells*, *190* (June 2018), 6–11. https://doi.org/10.1016/j.solmat.2018.10.009

[52] M. Islam, M. Rahman, J. Podder, and S. Farhad, 'Structural, optical and photocatalysis properties of sol–gel deposited Al-doped ZnO thin films', *Surfaces and Interfaces*, vol. 16, 2019, doi: 10.1016/j.surfin.2019.05.007

[53] G. Petrucci, D. Caputo, A. Nascetti, N. Lovecchio, E. Parisi, S. Alameddine, G. de Cesare, A. Zahra, Thermal characterization of thin film heater for lab-on-chip application, in: 2015 XVIII AISEM Annu. Conf., IEEE, 2015, pp. 1–4, https://doi.org/10.1109/AISEM.2015.7066835

[54] B.W. An, E.-J. Gwak, K. Kim, Y.-C. Kim, J. Jang, J.-Y. Kim, J.-U. Park, Stretchable, transparent electrodes as wearable heaters using nanotrough networks of metallic glasses with superior mechanical properties and thermal stability, Nano Lett. 16 (2016) 471–478 https://doi.org/10.1021/acs.nanolett.5b04134

[55] Jayathilake, D. S. Y., Sagu, J. S., & Wijayantha, K. G. U. (2019). Transparent heater based on Al , Ga co-doped ZnO thin films. Materials Letters, 237, 249–252. https://doi.org/10.1016/j.matlet.2018.11.092

[56] S. Kurtaran, 'Al doped ZnO thin films obtained by spray pyrolysis technique : Influence of different annealing time', vol. 114, no. December 2020, pp. 20–25, 2021.

[57] S. Kurtaran, S. Aldaˇg, G. ¨Ofˇofoˇglu, I. Akyüz, F. Atay, On the role of Al in ultrasonically sprayed ZnO films, Mater. Chem. Phys. 185 (2017) 137–142.

[58] Y. Zhang, Z. Fei, H. Huang, T. Lü, and R. Mu, 'In fl uence of ZnO Cap Layer Morphology on the Electrical Properties and Thermal Stability of Al-Doped ZnO Films', vol. 2000025, pp. 1–7, 2020, doi: 10.1002/pssa.202000025.

[59] N. Kumar, A. Haider, B. Bahrami, and M. Reza, 'Origin of enhanced carrier mobility and electrical conductivity in seed-layer assisted sputtered grown Al doped ZnO thin fi lms', Thin Solid Films, vol. 700, no. May 2019, p. 137916, 2020, doi: 10.1016/j.tsf.2020.137916.

[60] K.N. Tonny, R. Rafique, A. Sharmin, M.S. Bashar, Z.H. Mahmood, Electrical, optical and structural properties of transparent conducting Al doped ZnO (AZO) deposited by sol-gel spin coating, AIP Adv. 8 (2018) 065307

[61] J.B. Kim, S.B. Jin, L. Wen, P. Premphet, K. Leksakul, J.G. Han, Low temperature, high conductivity Al-doped ZnO film fabrication using modified facing target sputtering, Thin Solid Films 587 (2015) 88–93.

[62] D.K. Kim, H.B. Kim, Room temperature deposition of Al-doped ZnO thin films on glass by RF magnetron sputtering under different Ar gas pressure, J. Alloy. Compd. 509 (2011) 421–425

[63] T. Yang, S. Song, Y. Li, Y. Xin, G. Du, M. Lv, S. Han, The enhanced conductivity and stability of AzO thin films with a TiO2 buffer layer, Physica B 407 (2012) 4518–4522

[64] P. Sagar, M. Kumar, R.M. Mehra, Influence of hydrogen incorporation in sol-gel derived aluminum doped ZnO thin films, Thin Solid Films 489 (2005) 94–98

[65] P.-.C. Yao, S.-.T. Hang, Y.-.S. Lin, W.-.T. Yen, Y.-.C. Lin, Optical and electrical characteristics of Al-doped

ZnO thin films prepared by aqueous phase deposition, Appl. Surf. Sci. 257 (2010) 1441–1448

[66] Y.-.S. Liu, C.-.Y. Hsieh, Y.-.J. Wu, Y.-.S. Wei, P.-.M. Lee, H.-.M. Hsieh, C.-.Y. Liu, Mechanism of conductivity degradation of AzO thin film in high humidity ambient, Appl. Surf. Sci. 282 (2013) 32–37

[67] Z.P. Kan, Z.W. Wang, Y. Firdaus, M. Babics, H.N. Alshareef, P.M. Beaujuge, Atomic- layer-deposited AzO outperforms ITO in high-efficiency polymer solar cells, J. Mater. Chem. A 6 (2018) 10176–10183.

[68] R.N. Chauhan, N. Tiwari, R.S. Anand, J. Kumar, Development of Al-doped ZnO thin film as a transparent cathode and anode for application in transparent organic light- emitting diodes, Rsc. Adv. 6 (2016) 86770–86781

[69] R.C. Raju Nagiri, S.D. Yambem, Q. Lin, P.L. Burn, P. Meredith, Room-temperature tilted-target sputtering deposition of highly transparent and low sheet resistance Al doped ZnO electrodes, J. Mater. Chem. C 3 (2015) 5322–5331

[70] A. Kumar and I. Ahmad, 'Role of defects and microstructure on the electrical properties of solution - processed Al - doped ZnO transparent conducting films', *Appl. Phys. A*, vol. 126, no. 8, pp. 1–11, 2020, doi: 10.1007/s00339-020-03767-0.

[80] K. Ellmer, J. Phys. D. Appl. Phys. 34, 3097 (2001)

[81] V. Devi, H. Pandey, D. Tripathi, M. Kumar, and B. C. Joshi, 'Optical and electrical properties of pristine and Al doped ZnO thin films Optical and Electrical Properties of Pristine and Al Doped ZnO Thin Films', vol. 040010, no. August, 2019.

[82] Dimitrov, Dimitre, Che-liang Tsai, Stefan Petrov, Vera Marinova, Dimitrina Petrova, Blagovest Napoleonov, and others, „Atomic Layer-Deposited Al-Doped ZnO Thin Films for Display Applications", 2020, 1–12 ,doi:10.3390/coatings10060539

[83] M.H. Hong, C.S. Park, W.S. Seo, Y.S. Lim, J.K. Lee, H.H. Park, < 2013 (2013) 131537

[84] H.F. Hussein, G.M. Shabeeb, S.S. Hashim, J. Mater. Environ. Sci. 2 (2011) 423

[85] Y. H. Kim, S. J. Kim, Y.-J. Kim, Y.-S. Shim, S. Y. Kim, B. H. Hong, H. W. Jang, ACS Nano 2015, 9, 10453

[86] C. Gong, Y. Zhang, W. Chen, J. Chu, T. Lei, J. Pu, L. Dai, C. Wu, Y. Cheng, T. Zhai, L. Li, J. Xiong, Adv. Sci. 2017, 4, 1700231

[87] B. Cho, M. G. Hahm, M. Choi, J. Yoon, A. R. Kim, Y.-J. Lee, S.-G. Park, J.-D. Kwon, C. S. Kim, M. Song, Y. Jeong, K.-S. Nam, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, H. C. Ko, P. M. Ajayan, D.-H. Kim, Sci. Rep. 2015, 5, 8052

[88] H. Y. Jeong, D.-S. Lee, H. K. Choi, D. H. Lee, J.-E. Kim, J. Y. Lee, W. J. Lee, S. O. Kim, S.-Y. Choi, Appl. Phys. Lett. 2010, 96, 213105

[89] W. Yuan, A. Liu, L. Huang, C. Li, G. Shi, Adv. Mater. 2013, 25, 766.

[90] T. Kim, Y. Kim, S. Park, S. Kim, H. Jang, Chemosensors 2017, 5, 15.

[91] I. V. Zaporotskova, N. P. Boroznina, Y. N. Parkhomenko, L. V. Kozhitov, Mod. Electron. Mater. 2016, 2, 95

[92] S. S. Varghese, S. Lonkar, K. K. Singh, S. Swaminathan, A. Abdala, Sens. Actuators, B 2015, 218, 160

[93] C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, Sensors 2010, 10, 2088 6

[94] P. Shankar, J. B. B. Rayappan, J. Mater. Chem. C 2017, 5, 10869

[95] Zhang, X. Liu, G. Neri, N. Pinna, Adv. Sci. 2016, 28, 795

[96] A. Sanger et al., "Morphology-Controlled Aluminum-Doped Zinc Oxide Nanofibers for Highly Sensitive NO_2 Sensors with Full Recovery at Room Temperature", vol. 1800816, no. 2, 2018, doi: 10.1002/advs.201800816.

[97] P. S. Kolhe, A. B. Shinde, S. G. Kulkarni, N. Maiti, P. M. Koinkar, and K. M. Sonawane, „Gas sensing performance of Al doped ZnO thin fi lm for H 2 S detection", J. Alloys Compd., vol. 748, pp. 6–11, 2018, doi: 10.1016/j.jallcom.2018.03.123.

[98] Kathwate, L. H., Umadevi, G., Kulal, P. M., Nagaraju, P., Dubal, D. P., Nanjundan, A. K., & Mote, V. D. (2020). Ammonia gas sensing properties of Al doped ZnO thin films. Sensors and Actuators, A: https://doi.org/10.1016/j.sna.2020.112193 Physical, 313, 112193.

[99] S. Bai, T. Guo, Y. Zhao, R. Luo, D. Li, A. Chen, C.C. Liu, J. Mater. Chem. A 1 (2013) 11335–11342

[100] U. Chaitra, A. V. M. Ali, A. E. Viegas, D. Kekuda, and K. M. Rao, „Growth and characterization of undoped and aluminium doped zinc oxide thin films for SO2 gas sensing below threshold value limit", Appl. Surf. Sci., vol. 496, no. August, p. 143724, 2019, doi: 10.1016/j.apsusc.2019.143724.

[101] S. Kundu, R. Majumder, R. Ghosh, and M. Pal Chowdhury, „Superior positive relative humidity sensing properties of porous nanostructured Al:ZnO thin films deposited by jet- atomizer spray pyrolysis technique", J. Mater. Sci. Mater. Electron., vol. 30, no. 5, pp. 4618–4625, 2019, doi: 10.1007/s10854-019-00754-x

[102] H. Aydın, F. Yakuphanoglu, and C. Aydın, „Al-doped ZnO as a multifunctional nanomaterial: Structural, morphological, optical and low-temperature gas

sensing properties", J. Alloys Compd., vol. 773, pp. 802–811, 2019, doi: 10.1016/j.jallcom.2018.09.327

[103] Namgung, Q. T. H. Ta, W. Yang, and J. S. Noh, „Diffusion-Driven Al-Doping of ZnO Nanorods and Stretchable Gas Sensors Made of Doped ZnO Nanorods/Ag Nanowires Bilayers", ACS Appl. Mater. Interfaces, vol. 11, no. 1, pp. 1411–1419, 2019, doi: 10.1021/acsami.8b17336

[104] T. Krishnakumar et al., „CO gas sensing of ZnO nanostructures synthesized by an assisted microwave wet chemical route", Sensors Actuators, B Chem., vol. 143, no. 1, pp. 198–204, 2009, doi: 10.1016/j.snb.2009.09.039.

[105] A. Sharmin, S. Tabassum, M. S. Bashar, and Z. H. Mahmood, „Depositions and characterization of sol–gel processed Al-doped ZnO (AZO) as transparent conducting oxide (TCO) for solar cell application", J. Theor. Appl. Phys., vol. 13, no. 2, pp. 123–132, 2019, doi: 10.1007/s40094-019-0329-0

[106] S. Ghosh, A. Mallick, B. Dou, M. F. A. M. van Hest, S. M. Garner, and D. Basak, „A novel blanket annealing process to achieve highly transparent and conducting Al doped ZnO thin films: Its mechanism and application in perovskite solar cells", Sol. Energy, vol. 174, no. April, pp. 815–825, 2018, doi: 10.1016/j.solener.2018.09.017

[107] G. Namgung, Q. T. H. Ta, W. Yang, and J. S. Noh, „Diffusion-Driven Al-Doping of ZnO Nanorods and Stretchable Gas Sensors Made of Doped ZnO Nanorods/Ag Nanowires Bilayers", ACS Appl. Mater. Interfaces, vol. 11, no. 1, pp. 1411–1419, 2019, doi: 10.1021/acsami.8b17336

[108] R. Nisha, K. N. Madhusoodanan, T. V. Vimalkumar, and K. P. Vijayakumar, „Gas sensing application of nanocrystalline zinc oxide thin films prepared by spray pyrolysis", Bull. Mater. Sci., vol. 38, no. 3, pp. 583–591, 2015, doi: 10.1007/s12034-015-0911-2.

[109] S. O. El Hamali, W. M. Cranton, N. Kalfagiannis, X. Hou, R. Ranson, and D. C. Koutsogeorgis, „Enhanced electrical and optical properties of room temperature deposited Aluminium doped Zinc Oxide (AZO) thin films by excimer laser annealing", Opt. Lasers Eng., vol. 80, pp. 45–51, 2016, doi: 10.1016/j.optlaseng.2015.12.010.