

Review of ZnO Nano Devices

H. Murad, M. Abdulrahman, Y. Saleh, Ahmed M. Nahhas*

Department of Electrical Engineering, Faculty of Engineering and Islamic Architecture,
Umm Al Qura University, Makkah, Saudi Arabia
*Corresponding author: anahhas@hotmail.com

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Abstract This paper presents the advances of Zinc Oxide (ZnO) devices. Due to its unique properties, ZnO has gained a substantial intension in the advancement of semiconductor-device technologies. ZnO is considered as one of the major candidates for several electronic and photonic applications. Many research has been conducted about ZnO and its contributions in several high-tech semiconductors fabrications that will take the technology of electronics to a higher level in several applications. ZnO nanostructured material can absorb UV radiation. ZnO nanowires have received considerable attention due to the morphological changes with doping. ZnO nanowires are very attractive material for nano-sensors due to their properties induced by the quantum size effects. Recently, ZnO nanowires-based devices have gained much attention due to their various potential applications in nanoelectronics devices including gas sensors, nanogenerators, and nano-lasers. This paper presents and discusses the importance of ZnO in the advancement of nanowire-based gas sensors. Applications of the ZnO in technology in solar cells will be introduced as well in addition to other applications and designs of other devices such as UV-photodetection and Nanorods application in wave transmissions.

Keywords: Zinc Oxide, Nanostructured, Doping, LEDs, Nanowires, UV, Sensors, X-RAY DIFFRACTION (XRD)

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1. Introduction

ZnO is an *n*-type semiconductor material, falls in group II-VI [1]. Like other semiconductors, ZnO has dual properties of both conductors and insulators [1]. Its electrical properties are controllable via doping processes [1]. ZnO has a wide band gap of 3.37 eV compared to 1.1 eV in silicon. ZnO has other interesting properties such as high exciton binding energy, thermal stability, environmental compatibility, high mechanical and optical gain, and radiation hardness [2]. These properties made ZnO a leading material for several electronic and optoelectronic devices [1]. The high binding energy permits the fabrication of ZnO based photo- electronic devices possessing high optical efficiency, while the wide band gap eases the application of ZnO thin films for short wavelength optoelectronic devices [3].

The doping of ZnO nanowires improves their electrical and optical properties. ZnO nanowires can be doped with Al, Ga, Sb, Ag, Cu, As, and Mo [1]. ZnO nanowires have attracted extensive research interests for their potential applications in optoelectronic areas. In recent years, many research have reported on devices based on ZnO nanostructured nanowires because of their high specific surface area, low cost, and ease of manufacturing [1]. Due to the mentioned properties and others, ZnO is selected in several applications in the development of high- performance semiconductor devices [1]. In specific,

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The ZnO crystalline structure exists as wurtzite and zinc blende as shown in Figure 1, which led it as a perfect polar symmetry along the hexagonal axis, which is responsible for several the physical and chemical properties, including piezoelectricity and spontaneous polarization [4].

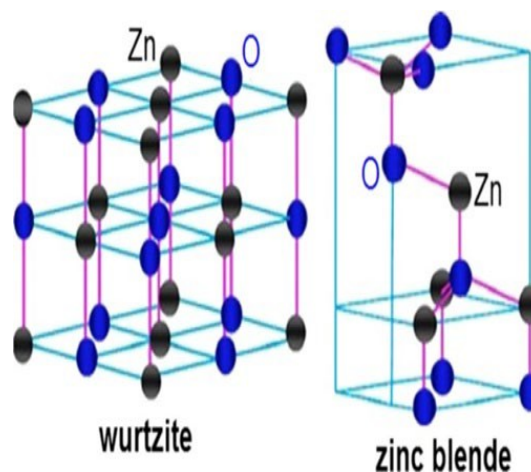


Figure 1. ZnO structures [1,4]

2. ZnO Doping

It is important while discussing ZnO-based devices to highlight some guidelines of the doping processes of ZnO nanowires enabling the designer to be aware of the doping limitations [1]. The doping processes of ZnO nanowires were investigated and reported by Nahhas [1]. The doping of ZnO nanowires improves their electrical and optical properties. ZnO nanowires can be doped with Al, Ga, Sb, Ag, Cu, As, and Mo [5]. Both *n*-type and *p*-type doping of ZnO nanowires has been realized: typical *n*-type dopants include Al, Ga, Sb; *p*-type dopants include as [1]. Normally, ZnO is an *n*-type as grown [6]. The intrinsic ZnO is *n*-type due to oxygen vacancies and thus, doping it with *p*-type dopants has proven to be extremely difficult. However, that work has shown that *p*-type impurities can potentially reduce the charge leakage and electron screening effect [7]. Among the *p*-type dopants, Li is an excellent candidate because it can take off centered positions by replacing Zn atoms in the Wurtzite structure [8]. ZnO epilayers are usually found to be unintentionally *n*-type conducting with high electron concentration. This is believed to be resulting of certain point defects [9]. This is one of the reasons for a reliable and reproducible *p*-type ZnO film is difficult to achieve. The *p*-type doping is considered one of the biggest issues to the development of ZnO based *p-n* junction devices. GaN is one of the materials that can be used to bypass this issue without sacrificing the advantages of a ZnO material [10]. GaN is a wide band gap semiconductor with a very similar lattice constant as ZnO and where *p*-type doping can be reliably achieved with Mg doping, in place of *p*-ZnO [10]. In many applications, the *p*-type doping of ZnO is desired such as *p-n* heterojunction structure. There are several reports on ZnO- based heterojunctions with *p*-type semiconductors such as Si [11], AlGaIn [12], or GaN [13]. On the other hand, doping of ZnO with group III elements like Aluminum (Al) [14], Gallium (Ga) [15], and Indium (In) [16] is known to decrease the electrical resistivity significantly caused by an increased free carrier concentration. Al is used for doping due to its nontoxic, inexpensive with high conductance and high transparent in visible range [14].

3. ZnO Nano Powders

Another interesting ZnO nano particle is Nano powder. Nano powder existence within ZnO enabled advancement of devices. The improvement of varistor devices with a ZnO based material was investigated and reported by Boumezoued et al [17]. In that work, the study of the impact of sintering temperature on the performance of ZnO-Bi₂O₃ varistors through the synthesis and characterization of ZnO-based nano powders. The goal is pure and 1% Bi-doped ZnO nano-powders have been synthesized at different sintering temperatures by a soft chemistry method: the sol-gel route [18]. The used temperatures were carefully chosen to obtain the desired phases: (a-Bi₂O₃, b-Bi₂O₃, and d-Bi₂O₃). Characterizations were made by XRD and TEM to determine the structural properties and particle sizes of Bi phases [19]. XRD

spectra confirmed the wurtzite structure and the presence of many transition phases for each sintering temperatures with an average grain size varying from 42 nm to 76 nm [20]. TEM and SEM images of the samples allowed to study the location of different phases, their morphologies, and the size of particles, and they show a mixture of nano-objects of different sizes and shapes [21]. The electrical characteristics J(E) were measured to correlate those results with the varistor effect which indicate a good nonohmic behavior for all samples; the threshold voltage VB ranges between 242 and 701 V/cm and the coefficient of nonlinearity between 10.26 and 14.5 [22,23]. The total absence of phase transitions between the grains of the triple point in the ZnO-Bi₂O₃-based varistor is presented [24]. Moreover, it has been shown that most phase transitions are located at the boundary of grains and forms a Schottky barrier which is suitable to improve the protective effect of surge arresters for hugely suppressing over-voltages in power and network systems [25].

4. ZnO Nanoscale Interface

Future electronics that are powering the next phase of the digital transition will require the thin-film transistor (TFT), a crucial component. Detailed study and investigation were performed by Ravindra et al [26,27]. Their work presented advancement of one of the most advantageous developments for large-area flexible electronics of the future is the development of metal-oxide-semiconductor (MOS) TFTs [28]. The systematic examination of amorphous gallium oxide (a-Ga₂O₃) and its use in nanocrystalline ZnO TFTs is demonstrated in this paragraph [29]. The TFT with a Ga₂O₃/c-ZnO-stack channel displays outstanding stability under positive-bias-temperature stress and a field-effect mobility of 41 cm² V⁻¹ s⁻¹ [30]. Upon 100k bending cycles with a radius of 3 mm, the a-Ga₂O₃/c-ZnO-stack TFT on polyimide (PI) substrate demonstrates a small threshold voltage shift and is very stable under environmental testing [31]. The charge transport in Ga₂O₃/ZnO-stack TFT is improved by the smooth morphology with tiny grains that are about 12 nm in diameter and have less grain boundary states [32]. The heterointerfaces are improved and the defect density in the Ga₂O₃/ZnO interface is reduced by the presence of amorphous a-Ga₂O₃ between very thin ZnO layers [33]. Because of this, adding a-Ga₂O₃ to stacked TFTs can improve stability and mobility for next-generation flexible TFT devices [34,35,36].

5. ZnO Nanoparticles Electrical Conductivity

Nanotechnology is the process of creating materials at nanoscales (10-9 nm) with unique properties derived from bulk materials. One class of applications for nanofluid has been reported for its usage in fuel cell and electronic device cooling as thermal management. Research in nanotechnology has demonstrated long-term benefits for a variety of fields, including engineering and medical science are studying the electrical conductivity of ZnO

nanofluids based on aqueous glycol [37,38]. The work reported by Chilambarasan et al most of the literature on nano-suspensions, electrical conductivity investigations were utilized as the basis to determine the stability of nano-suspensions. In that paper, two glycol-based nanofluids dispersed with ZnO nanoparticles with an average diameter of 50 nm were studied for electrical conductivity in the temperature range of 30-55°C [39]. The ZnO nanoparticles were added to the (30 EG: 70 Water) and (30 PG: 70 Water) composition-prepared aqueous glycol base fluid at a low volume concentration of 0.01 to 0.05%. The electrical conductivity (EC) of nanofluids were predicted with temperature using experimental results for each volume concentration [40,41,42]. According to the data, aqueous propylene glycol's electrical conductivity decreased when ZnO nanoparticles were added (except at 0.04% volume concentration), whereas aqueous ethylene glycol exhibited the opposite behavior [43]. At volume concentrations of 0.04% and 0.01% at 550°C, respectively, electrical conductivity

enhancements of up to 20% and 12% were achieved for aqueous propylene and ethylene glycol nanofluids [44]. At all volume concentrations, both nanofluids exhibited a temperature-dependent increase in electrical conductivity [45].

6. ZnO Nanowires Devices

ZnO nanowires have attracted extensive research interests for their potential applications in optoelectronic areas. In recent years, many research have reported on devices based on ZnO nanostructured nanowires because of their high specific surface area, low cost and ease of manufacturing [1,46,47,48,49]. Several methods are being used for the synthesis of ZnO nanowires such as vapor liquid solid [50], metal organic chemical vapor deposition [51], chemical bath deposition [52] and hydrothermal method [53]. The quality of the resulted ZnO nanowires fabricated by these methods are varied [1].

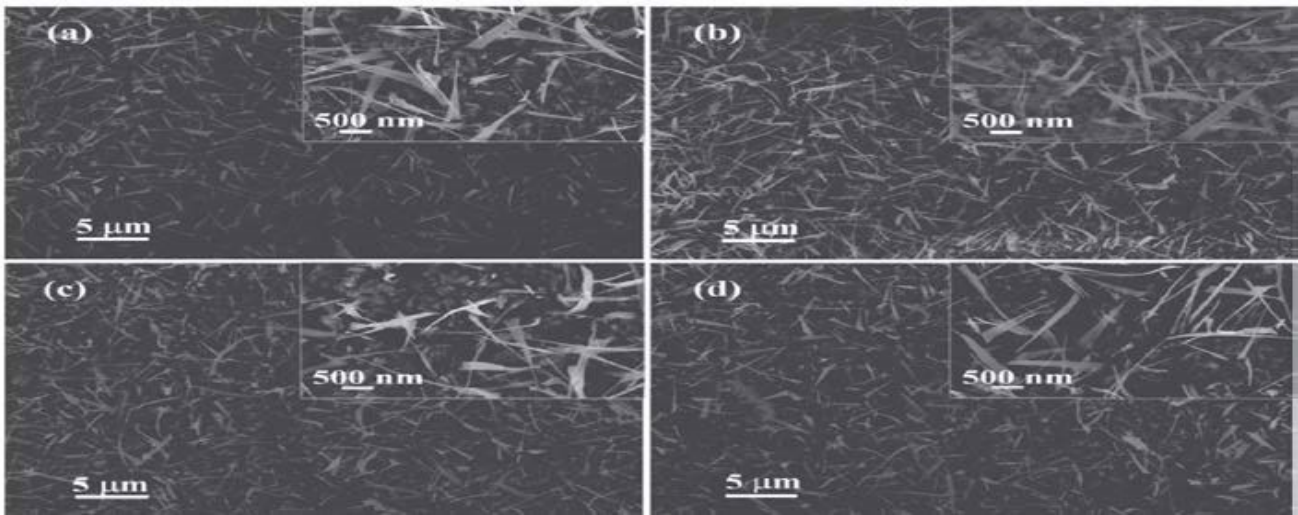


Figure 2. Electrical characteristic of the individual nanowire and the nanowires conductivities before and after tetrafluoromethane plasma treatments at different bias voltages [1]

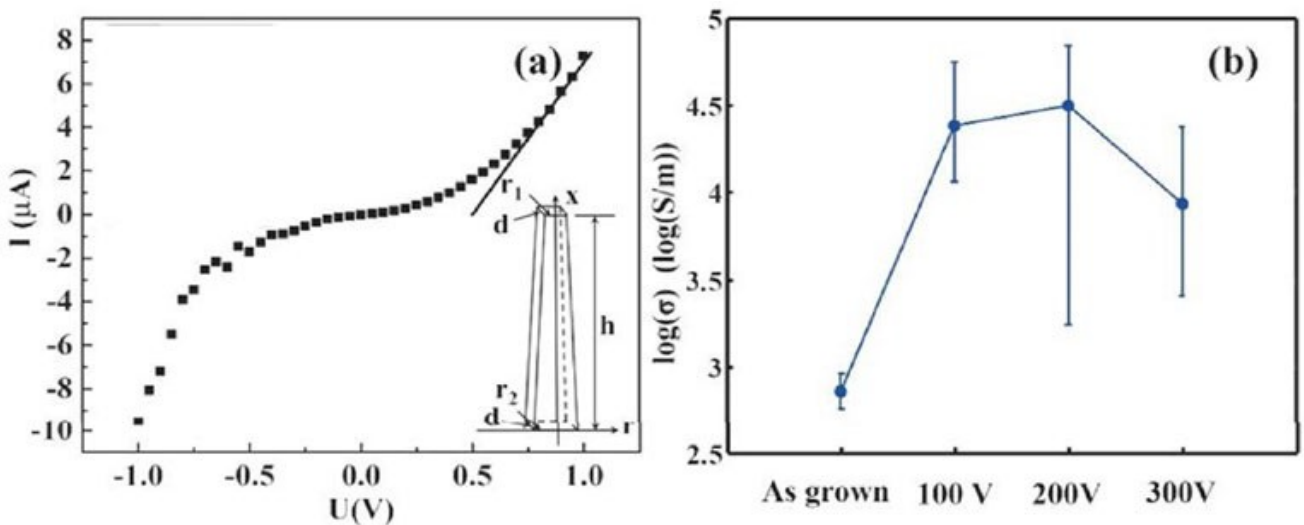


Figure 3. SEM images of (a) as-grown ZnO nanowires and tetrafluoromethane plasma treated nanowires with bias voltages of (b) 100, (c) 200, and (d) 300 V. The insets show corresponding high magnification SEM images [1]

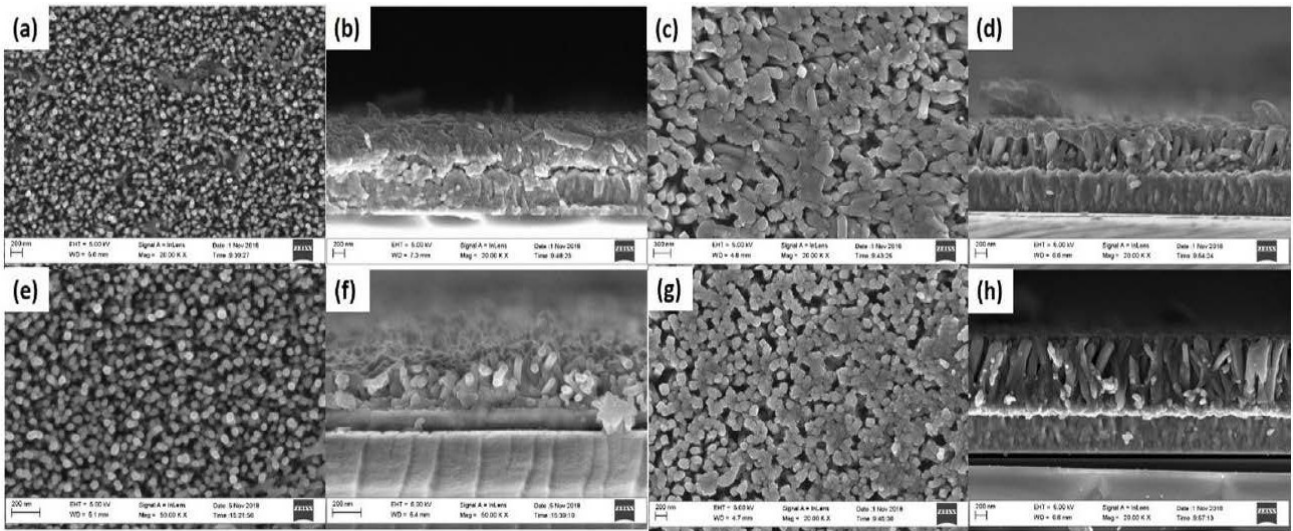


Figure 4. SEM micrographs of (a, b) TiO₂; (c, d) N-TiO₂ (e, f) ZnO and (g, h) N-ZnO nanowires [51]

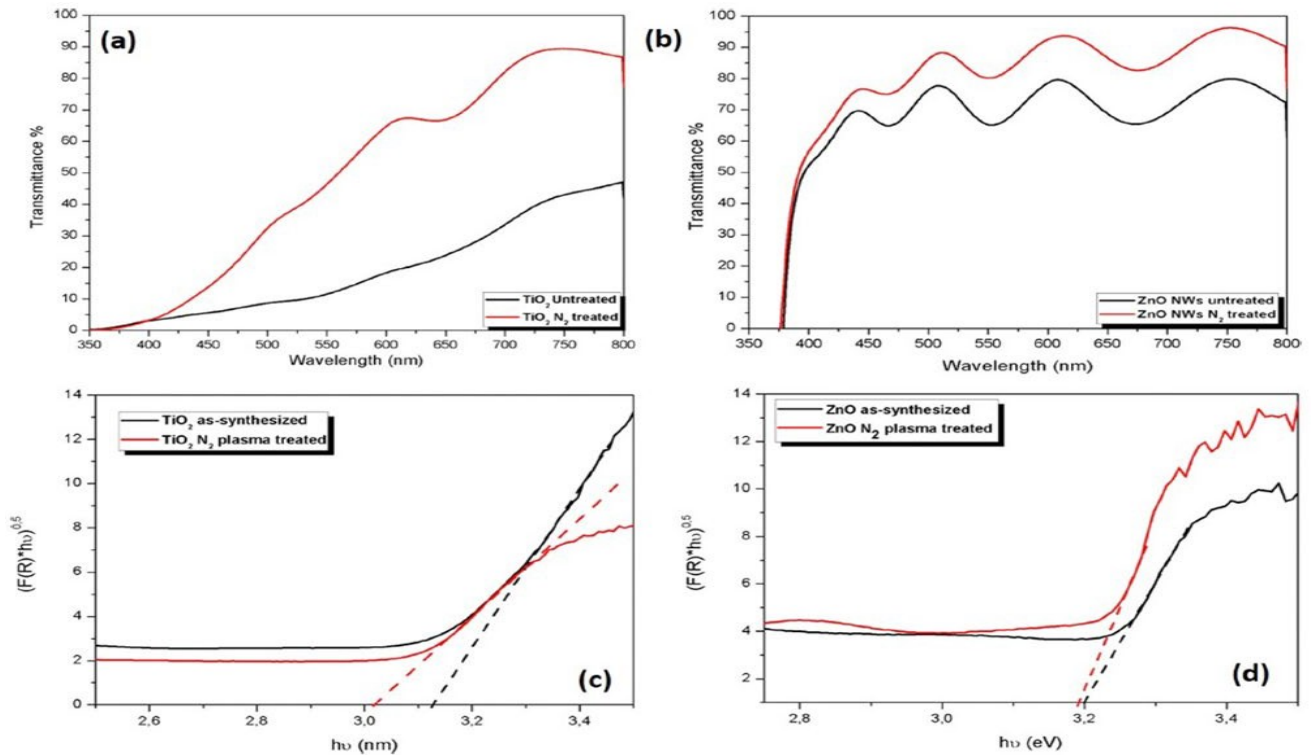


Figure 5. UV-vis transmittance plots of untreated versus N₂ plasma treated (a) TiO₂ and (b) ZnO nanowires films; Tauc plots comparing the untreated and N₂ plasma treated structures of (c) TiO₂ and (d) ZnO [54]

The electrical properties of the fluorine doped ZnO nanowires were investigated and reported by Wang et al. [1,5]. The doping was used for tuning the electrical properties of ZnO nanowires [1,5]. In that study, the ZnO nanowires were prepared by a thermal oxidation method [1,5]. The fluorine doping was achieved by a biased plasma treatment, with bias voltages of 100, 200, and 300 V [1,5]. The resulted ZnO nanowires were tested by the transmission electron microscopy (TEM) indicated that the nanowires treated at bias voltages of 100 and 200 V featured low crystallinity [1,5]. The study results showed that the bias voltage was 300 V, the nanowires showed single crystalline structures [1,5]. The study showed that the photoluminescence measurements revealed that concentrations of oxygen and surface defects decreased at

high bias voltage [1,5]. The resulting structure was examined by XRD and SEM. The XRD photoelectron spectroscopy suggested that the F content increased as the bias voltage was increased [1,5]. The study results showed that the conductivity improvements of the nanowires formed at bias voltages of 100 and 200 V, were attributed to F-doping, defects, and surface states [1,5]. The conductivity of the ZnO nanowires treated at 300 V was attributed to the presence of F-ions [1,5]. Figure 2 shows the electrical characteristic of the individual nanowire and the nanowires conductivities before and after tetrafluoromethane plasma treatments at different bias voltages. Figure 3 shows the SEM images of the as-grown ZnO nanowires and tetrafluoromethane plasma treated nanowires with different bias voltages.

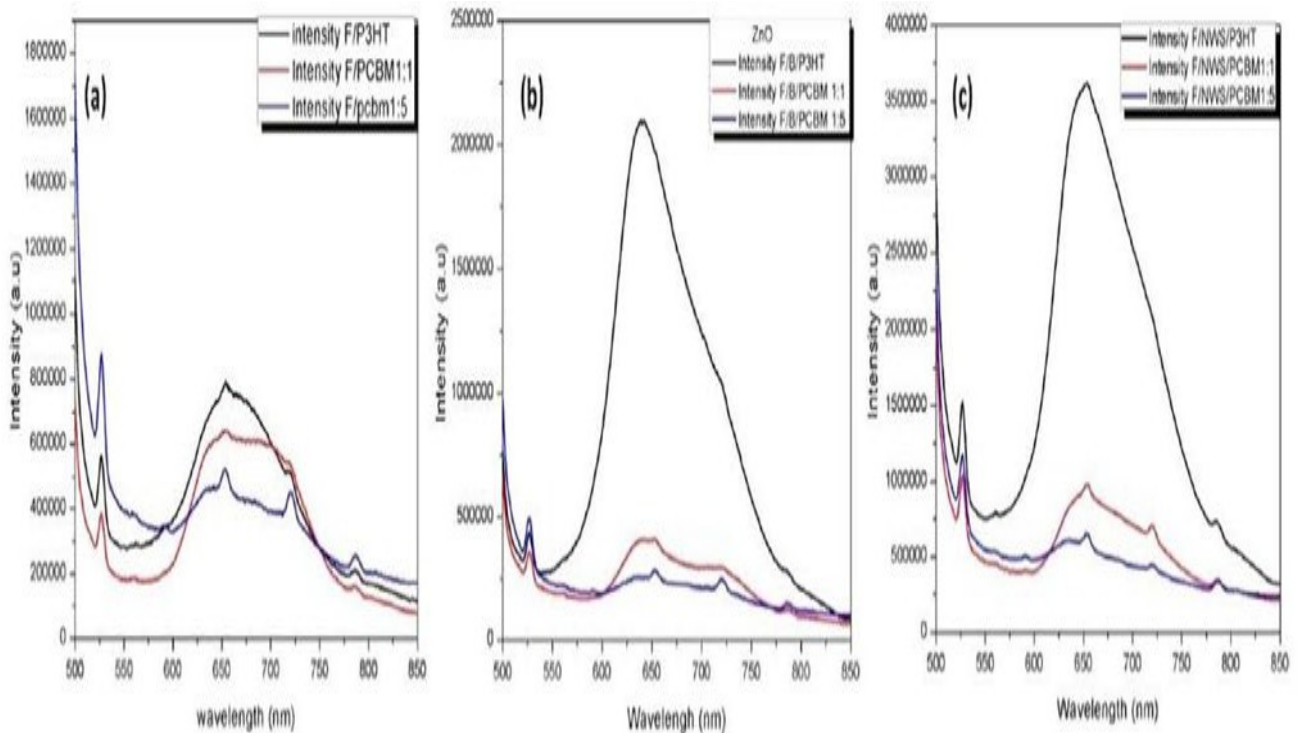


Figure 6. PL of the P₃HT: PCBM blends (a) without ETL; (b) with addition of a N-ZnO compact layer as an ETL; (c) ZnO nanowires array as an ETL [54]

The improved opto-electronic properties of the vertically aligned arrays of rutile TiO₂ and ZnO nanowires by means of controlled nitrogen doping during exposure to highly kinetic RF generated N₂ plasma radicals were investigated and reported by Muhammad et al. [54]. In that study, the plasma treatment caused a distortion of the vertical alignment of the nanowires due to a dissociation of the weak Van der Waals force clustering the nanowires [54]. The study results showed that the optical spectroscopy showed that plasma treatment increases the light transmission of TiO₂ arrays from 48% to 90%, with the ZnO arrays exhibiting an increase from 70% to 90% in the visible to UV range [54]. It also showed that the as-synthesized TiO₂ array had an indirect band gap of 3.13 eV, which reduces to 3.03 eV after N₂ treatment, with the ZnO equivalent decreasing from 3.20 to 3.17 eV post plasma exposure [54]. The resulted structures in P₃HT:PCBM polymer blended the photoluminescence quenching of the photoactive layer was significantly improved for both as-prepared and nitrogen-doped nanowires, thus making it an interesting and promising architecture for overall device efficiency improvement [54]. Figure 4 shows the SEM TiO₂, N-TiO₂, ZnO and N-ZnO nanowires. Figure 5 shows the UV-vis transmittance plots of the untreated versus N₂ plasma treated for TiO₂ and ZnO nanowires films. Figure 6 shows the PL comparing quenching behavior of the P₃HT:PCBM blends without an electron transport layer (ETL) and with the addition of a N-ZnO compact layer as an ETL, and, ZnO nanowires array as an ETL [1].

6.1. ZnO Based Sensors

Based on a nanocomposite of 5, 10, 15, 20 Tetraphenylporphyrinatonicel (TPPNi) and ZnO, this

integrated capacitive-and-resistive-type bimodal relative humidity sensor [55]. This work was investigated by Rizwan et al. [55]. The development of high-performance humidity sensors for a wide range of applications, from agriculture to intelligent medical monitoring systems, necessitates the use of a dependable and ultrasensitive sensing material [56]. A bimodal (capacitive and resistive) surface-type sensor was a popular choice for device fabrication due to its simple device architecture, robust quantification of ambient relative humidity (% RH), and compatibility with modern integrated circuit technology [57]. They proposed and demonstrated a simple fabrication method for a 5,10,15,20-(TPPNi-ZnO) nano [58]. Composite-based bimodal surface-type % RH sensor in that work [59]. The TPPNi macromolecule and ZnO nanoparticles were created using an environmentally friendly microwave-assisted technique and a thermally efficient chemical precipitation method, respectively. The Morphological study suggested that increasing the specific surface area of the TPPNi micro-pyramidal structures with ZnO nanoparticles may improve the sensing properties of the fabricated humidity sensor [60]. The sensor's capacitive and resistive relative humidity sensing characteristics had been monitored in the 40-85% relative humidity (% RH) bandwidth. Under biasing conditions of 1V of applied bias (V_{rms}) and 500 Hz AC test frequency, the fabricated sensor had a significantly higher sensitivity of 387.03 pF/% RH and 95.79 k/% RH in bimodal operation [61]. The capacitive sensor's average response and recovery times had been estimated to be 30 seconds [62]. It has also been discussed why such a high degree of sensitivity and significant reduction in response and recovery time were achieved [63]. Furthermore, the TPPNi-ZnO nanocomposite's intense and broad bandwidth spectral

response suggests that it could be used as a potential light-harvesting heterostructure nanohybrid in future studies [64]. Figure 7 shows the whole work.

Another interesting research by Eleonora et al are presented here which is investigating the control of Strain in a Ga-Doped ZnO Epilayer-Based NO Gas Sensor [65].

That work showed that the characteristics of gas sensors built on Ga-doped ZnO epilayers generated by metalorganic chemical vapor deposition with strain and dislocation control inside the active layer [66]. In terms of NO sensitivity, the gas sensor device based on a Ga-doped ZnO epilayer with a lower TEGa flow rate performs better than one based on a higher TEGa flow rate [67]. The greater dislocation density in the ZnO epilayer, which is interesting for future medical applications, may be caused by a lack of a Ga source throughout the film production process. High-resolution lattice pictures were used in that study to quantify the stain of the activated film, and samples with higher strain values exhibit stronger NO sensitivity than others [68]. The outcome was very pertinent to a suggested approach for strain quantification and was associated with the number of dangling bonds present inside the active layer. Finally, the proposed device's continued sensitivity at a NO gas concentration of 25 ppb was encouraging for potential medical applications [69].

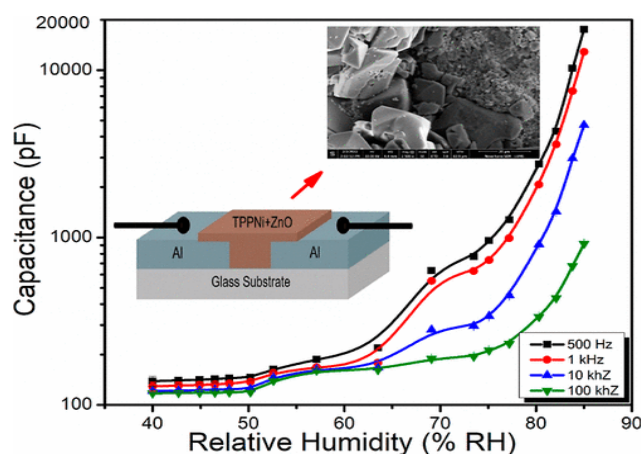


Figure 7. Nanocomposite of TPPNi and ZnO integrated capacitive-and-resistive-type bimodal relative humidity sensor

6.2. ZnO based Solar Cells

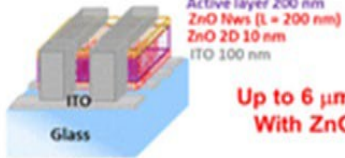
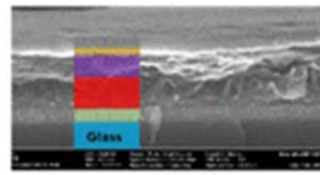
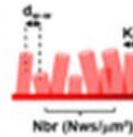
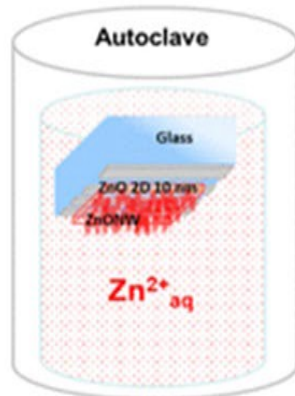
Solar cells have been demanding recently as the world is approaching maximizing the utilization of clean energy sources. Solar cells are being used for an intriguing approach for increasing photovoltaic conversion efficiency (PCE) [70]. That work was presented and investigated by Ali et al to create architected 3D hybrid photovoltaic solar cells that use ZnO nanowires as the electron transport layer (ETL) and nano collectors of electrons within the active layer of AL. The morphology of ZnO nanowires was meticulously controlled during the hydrothermal process [71]. Solar cells' AL was created by interconnecting ZnO nanowires with a bulk heterojunction made up of donor (-conjugate low band gap polymer: PBDD4T- 2F) and acceptor (fullerene derivate: PC71BM) materials [71]. A perfect interpenetrating ZnO nanowires - D/A system with

predefined morphological characteristics (length, diameter, and inter-ZnO nanowires distances) was designed and realized [72]. The 3D architectures based on dense ZnO nanowires arrays covered with conformal AL coatings result in increased ETL/AL interface, improved light absorption, and improved charge collection efficiency. Spin-coating at 100°C was discovered to be the best method for AL/ZnO nanowires assembly [73]. Other parameters, such as the D/A ratio and pre/post-treatments, were also optimized, yielding the optimal device with a D/A ratio of 1.25/1 and methanol treated ZnO nanowires before and after AL deposition. A PCE of 7.7% is achieved (1.4 times higher than in 2D cells) [74]. The improvement in performance with the 3D architecture is due to both (i) the improvement of the ZnO/AL surface interface (1 m²/m² for the 2D structure to 6.6 m²/m² for the 3D architecture); and (ii) the presence of ZnO nanowires inside the AL, which act as numerous nano collectors of electrons ZnO nanowires in the depth of the AL [75]. That result validated the efficacy of the nanotexturing of substrates concept, the method of solar cell assembly based on the nano-textured surface, the chosen morphological properties of the nanotexture, and the photoactive organic materials [76]. Figure 8 depicts the entire work.

6.3. ZnO Based Photodetectors

The engineering of novel miniaturized sensing materials that can quickly react to extremely minute changes in the concentration of biomarkers at room temperature is being driven by the rapid development of smart wearable devices. Although carbon-based nanomaterials have many desirable qualities, including low resistivity, good mechanical resilience, and integration potential, they are not well-suited for the detection and transmission of chemical molecules or photons [77]. Hanlem et al. presented the study of a three-dimensional nanostructured architecture for sensing volatile biomarkers at room temperature that consists of optimally integrated graphene oxide (GO)-ZnO hetero junctions [78]. The experiment demonstrated the layout's suitability as a visible-blind photodetector by demonstrating its good responsiveness to UV light [78]. Notably, optimum integration of evenly distributed GO nanodomains in a 3D ZnO network greatly improves the material's performance at room temperature in terms of chemical sensitivity and light responsivity, but greater GO concentrations significantly degrade it [79]. This was explained by the distinct functions that GO performs at low and high content [78,79]. Electron-depleted nano-heterojunctions with good electron-hole separation efficiency were created when small amounts of GO are used [80]. Large concentrations of GO, on the other hand, create a percolating electrical network that prevents the ZnO nanoparticles from sensing light and chemicals [80]. The ideal GO-ZnO exhibits 33 A W⁻¹ UV light responsiveness as well as the ability to detect volatile organic chemicals at ambient temperature down to 100 ppb. Those results offer guidance for the future design of hybrid carbon-metal oxide devices for a variety of uses, including optoelectronics, chemical sensing, and electrocatalysis [81]. Figure 9 shows the whole work.

ZnONW Synthesis



Up to $6 \mu\text{m}^2/\mu\text{m}^2$
With ZnONW

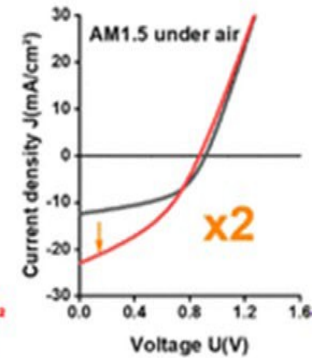


Figure 8. ZnO Nanowires for Effective Ambient Air-Processed Solar Cells: Custom Synthesis [89]

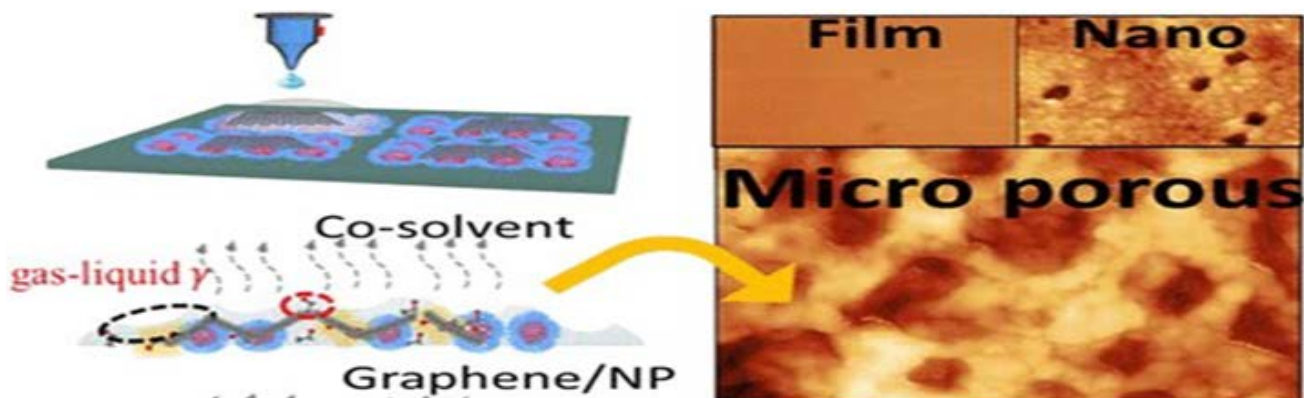


Figure 9. Nano-to-Microporous Networks for Ultraviolet Photodetectors Using Inkjet Printing of ZnO Nanoparticles/Graphene Hybrid [89]

Another interesting work in photodetection technology was reported by [82]. That work investigated the concept of Nano-to-Microporous networks for UV photodetectors using inkjet printing of ZnO Nanoparticles/Graphene hybrid. Over the past ten years, inkjet-printed photodetectors have attracted a lot of attention [83]. However, without postprocessing like annealing and UV treatment, device performance is constrained [83]. In addition, the restricted selection of low- viscosity ink solutions make it challenging to modify the surface morphology of the printed film using an inkjet printer. To create a high-performance ZnO-based photodetector on a flexible substrate, that work used an approach incorporating the control of the inkjet-printed film morphology via modification of cosolvent vapor pressure and surface tension. It was discovered that the film shape was influenced by the solvent boiling point across various cosolvent systems, which produces diverse photo detectivity as well as photo response time. Different solvents were used to print ZnO-based photodetectors, which demonstrated a quick photo response in solvents with low boiling points due to the low carbon residue and a greater photo detectivity in solvent systems with high boiling points due to the porous structure. Both solid-liquid and gas-liquid surface tension differences were used to create the porous structure, and the ratio of two solvents or two nanomaterials affects how big the pores were, ranging from nano to micro [83]. A high-performance photodetector with a high photoresponsivity ($7.5 \cdot 10^2 \text{ AW}^{-1}$)

and a quick photo response (0.18 s) can be made without the use of high-boiling point solvents because graphene's conductivity improves the transport behavior of the photocarrier [84].

Due to several defect-induced carriers, the detectivity of ZnO nanowire photodetectors was frequently constrained by a significant dark current.

The resultant alloyed nanoparticles have a maximum energy gap for ZnO-based solution processed nano-alloys to date of 4.35 eV, which is in the solar blind area.

In that work, a thin film of poly (2-vinyl naphthalene) (PVN) was positioned between the ZnO nanowire and gate dielectric to reduce the number of defect-induced carriers by using the electrostatic field created by trapped electrons in the PVN layer. Successfully lowered from $2.2 \cdot 10^{-9}$ to $1.6 \cdot 10^{-14}$ A was the dark current. Particularly, it was possible to create ZnO nanowire photodetectors with among the best recorded $I_{\text{light}}-I_{\text{dark}}$ ratios ($>10^7$), strong photoresponsivity ($>10^6 \text{ A W}_1$), and ultrahigh detectivity ($>10^{18}$ Jones). To decrease the dark current in semiconducting nanomaterials for ultrasensitive photo [1,85] detection applications, the proposed straightforward scheme offers a novel approach [85].

In terms of early warning, communication, and national security, the bandgap of semiconductors in the UV region, particularly in the solar-blind zone, has enormous promise [86]. That discussion was carried out by the researcher [86]. Due to their advantages in naturally large bandgaps, easy synthesis, and high exciton binding energy, ZnO-

based alloys such as ZnMgO have received a lot of interest [87]. However, at high alloying degrees, conventional techniques experience issues with phase separation and poor crystallinity [87]. The considerable strain on the 'c' axis brought on by the high Mg alloying degree is successfully relieved by adding Be ions to the ZnMgO nanoparticles, which restrict the crystal lattice [87]. The degree of Mg alloying then considerably increases as the critical ion concentration rises. Additionally, co-doping results in high crystallinity and low defect density while lowering the formation energy of nanoparticles with a high alloying degree [88]. With the help of this research, ZnO-based solar-blind optoelectronic devices will be made possible [89].

7. Conclusion

In conclusion, the recent advances of the ZnO based devices were presented and discussed. ZnO and its nano particles have been extensively studied over the past decade. Many great efforts have been intensified for understanding and utilizing the optical and electrical properties of ZnO. The ZnO based nanostructure configurations including nanoparticles have promising potential in several sensing and detection applications. Despite the sensing performances of the ZnO based nanostructured NO₂ sensors, there is still a problem of high operating temperature.

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