Review of Recent Advances of ZnO Nanowires Based Sensors

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Abstract This paper presents the recent advances of the ZnO nanowires based sensors. ZnO has gained a substantial interest in the research areas of the wide band gap semiconductors due to its unique electrical, optical and structural properties. ZnO is considered as one of the major candidates for several electronic and photonic applications. ZnO is considered as a potential contender in optoelectronic applications such as solar cells, surface acoustic wave devices, and ultraviolet (UV) emitters. ZnO as a nanostructured material exhibits many advantages for nanodevices. ZnO nanostructured material has the ability to absorb the UV radiation. ZnO nanowires have received a 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. The recent aspects of ZnO nanowires based sensors devices are presented and discussed.

Keywords: Zinc Oxide (ZnO), Nanostructured, Doping, LEDs, Nanowires, UV, Sensors

1. Introduction

ZnO is an n-type semiconductor material, falls in group II-VI [1]. It is in between covalent and ionic bond of semiconductor. ZnO has a wide band gap of 3.37 eV and high binding energy of 60 meV at room temperature [2]. Also, ZnO has some other interesting properties such as high exciton binding energy, thermal stability, environmental compatibility, high mechanical and optical gain, and radiation hardness [3]. These properties made ZnO a leading material for several electronic and optoelectronic devices. 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 [4].

ZnO has a good optical transparency in the visible wavelength region [5]. ZnO is considered as one of the major candidates for electronic and photonic applications due to its excellent optical and electrical characteristics. Due to its distinguishing features and interesting optoelectronic properties, ZnO is considered as a potential contender in optoelectronic applications such as solar cells, surface acoustic wave device, and UV emitters [6,7,8]. These characteristic properties attracted several researchers to improve the electrical and optical properties of ZnO thin films. Other physical properties opened a wide range of applications in photovoltaics, LEDs, photodetectors in UV spectral range, and microelectromechanical systems (MEMs) [9,10,11,12,13]. 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 a number of the physical and chemical properties, including piezoelectricity and spontaneous polarization [14].

Figure 1. ZnO structures [1,4]
2. ZnO Doping

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 [1,15]. 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 [16]. 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, p-type impurities can potentially reduce the charge leakage and electron screening effect [17]. 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 [18]. 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 [19]. 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 in order to bypass this issue without sacrificing the advantages of a ZnO material [20]. 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 [20]. 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 [21], AlGaN [22], or GaN [23]. On the other hand, doping of ZnO with group III elements like Aluminum (Al) [24], Gallium (Ga) [25], and Indium (In) [26] is known to decrease the electrical resistivity significantly caused by an increased free carrier concentration. The Al is used for doping due to its nontoxic, inexpensive with high conductance and high transparent in visible range [24].

3. ZnO Nanostructured Material

Recently, the deposition of the ZnO nanoscale materials with certain morphologies is increasing due to their novel optical and electrical properties and potential applications in the fields of photonic and electronic devices. Substantial efforts have been made for developing ZnO thin films in different shapes such as nanorods, nanowires, nanosprings, nanorings and nanobelts [27,28,29,30]. These nanostructured ZnO thin films have potential application in UV laser emission, biosensors, photodetectors, and LEDs devices. The nanostructured ZnO nanowires and nanorods based devices have attracted considerable interest due to their importance in potential applications such as electronic, optoelectronics, electrochemical, electromechanical nano devices [31] and biosensing [32]. Many other applications have been reported for the ZnO based nanostructures, thin films and devices, such as transparent electronics [33], UV light emitters [34], piezoelectric devices [35], p-n junctions [36], field effect devices [37], sensors [38], optoelectronics [39], and field emission devices [40].

4. ZnO Nanowires Devices

ZnO nanowires have attracted extensive research interests for their potential applications in optoelectronic areas. In recent years, many researches have reported on devices based on ZnO nanostructured nanowires because of their high specific surface area, low cost and ease of manufacturing [1,41,42,43,44]. Several methods are being used for the synthesis of ZnO nanowires such as vapor liquid solid [45], metal organic chemical vapor deposition [46], chemical bath deposition [47] and hydrothermal method [48]. The quality of the resulted ZnO nanowires fabricated by these methods is varied.

The electrical properties of the fluorine-doped ZnO nanowires were investigated and reported by Wang et al. [15]. The doping was used for tuning the electrical properties of ZnO nanowires [15]. In that study, the ZnO nanowires were prepared by a thermal oxidation method [15]. The fluorine doping was achieved by a biased plasma treatment, with bias voltages of 100, 200, and 300 V [15]. 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 [15]. The study results showed that the bias voltage was 300 V, the nanowires showed single crystalline structures [15]. The study showed that the photoluminescence measurements revealed that concentrations of oxygen and surface defects decreased at high bias voltage [15]. The resulted structure was examined by XRD and SEM. The X-ray photoelectron spectroscopy suggested that the F content increased as the bias voltage was increased [15]. 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 [15]. The conductivity of the ZnO nanowires treated at 300 V was attributed to the presence of F-ions [15]. Figure 2 shows the SEM images of the as-grown ZnO nanowires and tetrafluoromethane plasma treated nanowires with different bias voltages. Figure 3 shows the electrical characteristic of the individual nanowire and the nanowires conductivities before and after tetrafluoromethane plasma treatments at different bias voltages.

The improved opto-electronic properties of the vertically aligned arrays of rutile TiO$_2$ and ZnO nanowires by means of controlled nitrogen doping during exposure to highly kinetic RF generated N$_2$ plasma radicals was investigated and reported by Muhammad et al. [50]. 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 [50]. The study results showed that the optical spectroscopy showed that plasma treatment increases the light transmission of TiO$_2$ arrays from 48% to 90%, with the ZnO arrays exhibiting an increase from 70% to 90% in the visible to UV range [50]. It also showed that the as-synthesized TiO$_2$ array has an indirect band gap of 3.13 eV, which reduces to 3.03 eV after N$_2$ treatment, with the ZnO equivalent decreasing from 3.20 to 3.17 eV post plasma exposure [50]. The study showed that the resulted structures in P$_3$HT:PCBM polymer blends 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 [50]. 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.

Figure 2. 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 [15]

Figure 3. Electrical characteristic of individual ZnO nanowire (b) Statistical results of the nanowire conductivities before and after tetrafluoromethane plasma treatments at different bias voltages [15]

Figure 4. SEM micrographs of (a, b) TiO2; (c, d) N-TiO2; (e, f) ZnO and (g, h) N-ZnO nanowires [50]
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 [50]

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 [50]

5. ZnO Sensors Devices

The ZnO nanowires have attracted much interest in various optoelectronic nanoscale devices such as photovoltaic cells [51,52], UV laser diodes [53], LEDs, optical sensors, and UV photodetectors [54]. For many applications, it is preferable to have large surface area of ZnO. One of the simplest methods for increasing surface area is growing ZnO nanowires on the ZnO layers. The post-annealing process may affect the crystal structure as well as the photoluminescence spectra of ZnO nanorods [55]. ZnO nanorods can be fabricated by different methods including hydrothermal method [56], metal oxide chemical vapor deposition (MOCVD) method [57], pulsed laser deposition (PLD) method [58], aqueous solution method [59]. In these methods, the morphology, the microstructure, the optical and the electrical properties of ZnO nanowires are determined by process parameters such as deposition time, deposition temperature, and annealing condition. ZnO gas sensors play a crucial role for the monitoring of environmentally hazardous gases [60]. The development of the ZnO gas sensors has attracted great attention in the field of scientific research. The high response, fast response/recovery speed, and the outstanding selectivity are regarded as the most important parameters for designing gas sensors based on
semiconducting oxides [60]. Currently, ZnO with fast electron mobility as well as high exciton binding energy makes it very promising for gas detection [60]. Moreover, the surface morphologies and structural properties of ZnO can be readily modified by introducing changes during its synthesis process [60]. It has been known that the defects, grain size, and oxygen-adsorption quantities of ZnO will determine sensing response because of its sensing mechanism based on the surface-controlled properties [60].

The gas sensors based on the ZnO nanowire arrays/CuO nanospheres heterostructure was investigated and reported by Cai et al. [61]. The device was prepared by using the simple low temperature hydrothermal method [61]. The structure and surface morphology of the ZnO nanowire arrays/CuO nanospheres heterostructure was characterized by the X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (HRTEM) and energy dispersive spectrometry (EDX) were used to characterize the crystal phase, structure and surface morphology of the as-prepared samples, respectively [61]. The study’s results showed that the sensors based on the ZnO/CuO heterostructure exhibited excellent sensor parameters than pure CuO nanospheres [61]. The study also showed that a significant improvement of the gas sensing characteristics was related to the formation of PN heterojunction [61]. The study showed that the gas sensor exhibited broad application prospects in the detection of ethanol [61]. The obtained gas sensing performance demonstrated that the heterojunctions between the ZnO nanowire arrays and the CuO nanospheres played an important part in the sensing mechanism [61]. The ZnO/CuO heterostructure gas sensor could be used the detection of ethanol [61]. Figure 7 shows the FESEM and HRTEM for pure CuO. Figure 8 shows the response of the sensors based on pure CuO, ZnO, ZC-1, ZC-2 and ZC-3 to different target gases with a concentration of 100 ppm at the optimal operating temperature. Figure 9 shows the response/recovery time of the sensor based on the pure CuO, the ZC-2 to 80 ppm ethanol at the optimal operating temperature.

**Figure 7.** FESEM (a) and HRTEM (b) images of ZnO nanowires pure CuO [61]

**Figure 8.** Response of sensors based on pure CuO, ZnO, ZC-1, ZC-2 and ZC-3 to different target gases with a concentration of 100 ppm at the optimal operating temperature [61]

**Figure 9.** Response/recovery time of sensor based on (a) pure CuO, (b) ZC-2 to 80 ppm ethanol at optimal operating temperature [61]
The bare and palladium (Pd) functionalized ZnO nanowires were synthesized for hydrogen gas sensing was investigated and reported by Kim et al. [62]. The ZnO nanowires were fabricated by a vapor-liquid-solid technique and Pd functionalization was performed using an ultraviolet irradiation technique [62]. The study showed that the enhanced hydrogen gas response of the ZnO nanowires was observed after Pd functionalization [62]. Additionally, the Pd functionalized ZnO nanowires gas sensor exhibited a high selectivity to hydrogen gas [62]. The results of the study showed that the superior hydrogen gas sensing of the Pd functionalized ZnO nanowires sensor was related mainly to the sensitization of the Pd nanoparticles, metallization effect of ZnO at the sensing temperature (350 °C), and partial PdHx formation [62]. The results also showed that the effectiveness of the Pd functionalization on the ZnO nanowires for the realization of practical hydrogen gas sensors [62]. The hydrogen gas sensing results demonstrated the higher gas sensing capability of the Pd/ZnO nanowires relative to those of the bare ZnO while the Pd functionalized ZnO nanowires gas sensor exhibited a high selectivity [62]. The increased sensing response was due to the catalytic effects of the Pd nanoparticles, generation of Schottky contacts, and conversion to ohmic contacts upon the transition of Pd to a cleaner life environment [62].

Figure 10 shows the FESEM of the bare ZnO nanowires and Pd functionalized ZnO nanowires. Figure 11 shows the responses of the bare and Pd-functionalized ZnO nanowires sensors exposed to 100 ppm of hydrogen gas at different temperatures.

The impact of the carrier gas on the RT nitrogen dioxide sensing of the ZnO nanowire integrated film under UV illumination was investigated and reported by Zhou et al. [63]. In that study, the ZnO nanowire network sensor and UV-activated sensing performance toward trace nitrogen dioxide gas at RT of 25 °C was demonstrated [63]. In that study, the effect of the carrier gas (dry air and N2) on the sensing performance of the ZnO nanowires sensor was achieved [63]. In that study, two carrier gases were used dry nitrogen and air [63]. The N2 gas sensor exhibited a reversible response of 157 toward 50 ppb NO2 and a sensitivity of 7.8/ppb. Moreover, the decent selectivity and long-term stability were demonstrated [63]. The study results showed that after long-time UV exposure prior to the gas sensing tests within both carrier gas cases, the remaining oxygen ions were weakly bonded on ZnO surface, contributing to the reversible behaviors at room temperature [63]. The study results showed that the excellent long-term stability and selectivity were displayed in N2 case [63]. It also showed that the proposed sensing mechanism justified the reversible sensor behaviors especially under N2 atmosphere. Figure 12 shows the TEM and XRD for the ZnO nanowires. Figure 13 shows the energy band diagram of UV-assisted ZnO sensing at 25 °C.
The fabrication of 1D Zn$_2$SnO$_4$ nanowire and 2D ZnO nanosheet hybrid hierarchical structures for use in triethylamine gas sensors was investigated and reported by Liu et al. [64]. In that work, a unique Zn$_2$SnO$_4$-ZnO hierarchical structures composed of 1D Zn$_2$SnO$_4$ nanowires and two-dimensional ZnO nanosheets were successfully synthesized via a facile hydrothermal method combined with calcination [64]. The study showed that the Zn$_2$SnO$_4$ nanowires bridged across the ZnO nanosheets played an important role in electron transmission [64]. It also showed that the obtained Zn$_2$SnO$_4$-ZnO hierarchical structures exhibited improved gas sensing performance toward triethylamine (TEA) in terms of a low operating temperature, high sensor response, and good selectivity, comparing with pure Zn$_2$SnO$_4$ nanowires and pure ZnO nanosheets [64]. The results of the study showed that the gas sensing test results revealed that the sensor response of Zn$_2$SnO$_4$-ZnO sensor reached 175.5 toward 100 ppm TEA at an optimum operating temperature of 200 °C, which was approximately 47.4 and 30.8 times higher than that of pure Zn$_2$SnO$_4$ and pure ZnO, respectively [64]. In addition, the Zn$_2$SnO$_4$-ZnO hierarchical structures exhibited good selectivity and long-term stability toward TEA, suggesting their potential application in advanced TEA gas sensors [64]. The improved sensing properties of the Zn$_2$SnO$_4$-ZnO hierarchical structure could mainly be attributed to their large specific surface areas, unique bridged hierarchical microstructure, and appropriate energy band structure [64]. In addition, it was also found that the ZTO-ZnO exhibited good long-term working stability [64]. The enhanced gas sensing properties of the ZTO-ZnO sensors compared with pure ZnO were mainly ascribed to their large specific surface area, unique bridging structure, and appropriate energy band structure [64]. Figure 14 shows the SEM and HRTEM for ZTO-ZnO structures. Figure 15 shows the schematic illustration for the sensing mechanisms of the ZTO-ZnO structures toward TEA, the energy band diagrams of ZnO, ZTO, and the ZTO-ZnO.

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The selectivity shifting behavior of the Pd nanoparticles loaded zinc stannate/zinc oxide (Zn$_2$SnO$_4$/ZnO) nanowires sensors was investigated and reported by Arafat et al. [65]. In that study, the Zn$_2$SnO$_4$/ZnO and the Pd nanoparticles loaded Zn$_2$SnO$_4$/ZnO nanowires were synthesized for gas sensing applications [65]. That study constructed a 3D-like heterogeneous device integrated structure using a transparent ZnO nanowire MEMS gas sensor and a blue LED [65]. The ITO was used for the electrodes and the micro heater [65]. The thermal image showed that the micro heater provided a heat source [65]. The study showed that the sensors exhibited a higher sensitivity to NO than other gases (C$_2$H$_5$OH, HCHO, H$_2$S) at the optimal operating temperature of 200°C [65]. The results of the study showed that the blue light increased the carrier concentration in the ZnO nanowires [65]. The response value to 50 ppb NO gas was increased from 48.13% to 86.17% [65]. The study results also showed the Zn$_2$SnO$_4$/ZnO based sensors showed a selectivity towards C$_2$H$_5$OH gas when compared with H$_2$ and H$_2$S in N$_2$ background [65]. It also showed that the response time of the sensors was unaffected due to Pd loading on Zn$_2$SnO$_4$/ZnO nanowires. But, the recovery time of the sensors was reduced for loading of the Pd nanoparticles on Zn$_2$SnO$_4$/ZnO nanowires [65]. Figure 16 shows the FESEM images of the nanowires obtained by carbon assisted thermal evaporation process. Figure 17 shows the schematic representation of the band structure of Pd and Zn$_2$SnO$_4$ before and after contact.

The transparent ZnO nanowire MEMS gas sensor prepared by an ITO microheater was investigated and reported by Hsueh et al. [66]. In that study a 3D-like heterogeneous device integrated structure using a transparent ZnO nanowire MEMS gas sensor and a blue LED was constructed [66]. The ITO was used for the electrodes and the micro heater for the transparent gas sensor [66]. The thermal image showed that the micro heater provided a heat source [66]. The study showed that the sensors exhibited a higher sensitivity to NO than other gases (C$_2$H$_5$OH, HCHO, H$_2$S) at the optimal operating temperature of 200°C [66]. It also showed that the MEMS gas sensor with blue light illumination from the bottom of the sensors, showed that the blue light increased the carrier concentration in the ZnO nanowires [66]. The response value to 50 ppb NO gas was increased from 48.13% to 86.17% [66]. The results also showed that the ITO electrodes with a deeply etched area were illuminated from underneath with blue light to determine the effect on the sensors’ performance [66]. The result showed that the blue light increased the carrier concentration in the ZnO nanowires [66]. The study showed that the vertical integration of the gas sensors and LED’s was possible [66]. Figure 18 shows the 3D-like heterogeneous device with an integrated structure. Figure 19 shows the schematic diagram of the ZnO nanowire MEMS gas sensors from bottom to top, including the SiO$_2$ isolation layer, the ITO micro heaters, the ITO electrodes, the SiO$_2$ passivation layer and the hydrothermal synthesized ZnO nanowires. Figure 20 shows the infrared thermal images of the gas sensor at 200°C and the relationship between the applied voltage for the micro heater and the temperature of the sensing layer. Figure 21 shows the morphology of the sensor. Figure 22 shows the photograph of the blue light LED illumination from the underside of the MEMS sensor. Figure 23 shows the effect of the humidity and the long-term stability and reproducibility of the transparent ZnO nanowire MEMS gas sensor.
The enhanced NO$_2$ sensing performance of the ZnO nanowires functionalized with ultra-fine In$_2$O$_3$ nanoparticles was investigated and reported by Zhao et al. [67]. In that study the structure and the surface properties of the sensing materials have been recognized as the primary consideration for fabricating metal oxide semiconductor gas sensors [67]. In that study, the 1D ZnO nanowires with large length-to-diameter ratio were synthesized by a facile hydrothermal method and different contents of ultra-fine In$_2$O$_3$ nanoparticles were directly grown on their surface [67]. The resulted device structure was characterized by XRD, SEM, TEM, EDS, and XPS [67]. These techniques confirmed that the In$_2$O$_3$ nanoparticles were only 3-5 nm in diameter and well dispersed on the surface of ZnO nanowires [67]. The results of the study showed that the gas sensing showed that the ultra-fine In$_2$O$_3$ nanoparticles gave rise to a significant improvement in NO$_2$ response at their optimal operating temperature of 150°C [67]. The highest response of 54.6 to 1 ppm NO$_2$ was obtained for the sensor based on In$_2$O$_3$/ZnO composites with the In/Zn molar ratio of 5 %, which was about 8 times higher than that of pure ZnO nanowires [67]. It also showed that a high response of 18.4 to a relatively low NO$_2$ concentration of 250 ppb for In$_2$O$_3$-functionalized ZnO nanowires [67]. The results showed that the ZnO nanowires were 30-50 nm in diameter and 500 nm to several micrometers in length, while the In$_2$O$_3$ nanoparticles with the diameter of 3-5 nm were uniformly decorated on their surface [67]. In addition, the shorter response and recovery times were obtained by surface functionalization with ultra-fine In$_2$O$_3$ nanoparticles [67]. The significant enhancement in the NO$_2$ sensing performance may be attributed to the ultra-fine size of the In$_2$O$_3$ nanoparticles [67]. Figure 24 shows the fabrication process of ZnO gas sensor device. Figure 25 shows the SEM images of the ZnO nanowires. Figure 26 shows the NO$_2$ sensing process of In$_2$O$_3$ nanoparticles modified ZnO nanowires.
Figure 26. NO2 sensing process of In2O3 nanoparticles modified ZnO nanowires [67]

The synthesis of the ZnO nanowires Au nanoparticles hybrid was investigated and reported by Chen et al. [60]. In that study the device was made by facile one-pot hydrothermal method [60]. The enhanced NO2 sensing properties ZnO nanowires and ZnO nanowires Au nanoparticles hybrid with various Au concentrations were characterized by XRD, SEM, TEM, XPS, and FTIR [60]. The resulted structural characterization showed that Au nanoparticles were self-assembled onto the surface of nanowires and the c-axis growth of nanowires is suppressed by the addition of HAuCl4 in the synthesis of Au nanowire’s hybrid [60]. The study results showed that the gas sensing properties demonstrated the favorite sensing performance could be achieved for 1 mol% Au nanowires compared to pure nanowires and Au nanowires with other Au concentrations [60]. The Au nanowires with various Au concentrations showed better selectivity to NO2 than pure nanowires [60]. The study also showed that the mechanism of enhanced NO2 sensing properties for Au nanowires can be ascribed to the combination of electronic and chemical sensitizations via Au nanoparticle’s functionalization [60]. Figure 27 shows the XRD patterns of pure nanowires and Au nanowires with different Au concentrations. Figure 28 shows the FESEM images of pure ZnO nanowires. Figure 29 shows the responses of the sensors based on pure ZnO nanowires. Figure 30 shows the sensing mechanism of pure ZnO nanowires and Au-ZnO nanowires towards NO2.

Figure 27. XRD patterns of pure ZnO nanowires and Au-ZnO nanowires with different Au concentrations (a) Pure ZnO nanowires; (b) 1 mol% Au (c) 2 mol% Au (d) 5 mol% Au [60]

Figure 28. (a) FESEM images of pure ZnO nanowires (b) FESEM images of 2 mol% Au-ZnO nanowires [60]

Figure 29. Responses of ZnO sensors based on pure ZnO nanowires and Au-ZnO nanowires [60]

Figure 30. Sensing mechanism of pure ZnO nanowires and Au-ZnO nanowires towards NO2 (a) Pure ZnO nanowires in air; (b) Pure ZnO nanowires exposed to NO2; (c) Au-ZnO nanowires in air; (d) Au-ZnO nanowires exposed to NO2 [60]
The effects of the UV activation and surface oxygen vacancies on the room-temperature (RT) NO₂ gas sensing performance of the ZnO nanowires was investigated and reported by Wang et al. [68]. The study demonstrated the synergistic effects of the UV activation and surface VO on the RT NO₂ sensing performance of the ZnO nanowires [68]. The study showed that the ZnO was grown hydrothermally and treated in NaBH₄ solution to introduce rich surface VO [68]. The resulted RT NO₂ sensors showed significantly higher responses and faster response/recovery rates under the UV illumination compared with the VO deficient untreated [68]. The results also showed that the sensors exhibited excellent reversibility, high selectivity and good stability [68]. This was due to the improved optoelectronic properties as well as the UV and VO co-modulated surface chemisorption and reactions of Ox⁻ and NOx⁻ species [68]. Figure 31 shows the SEM images of the ZnO nanowires. Figure 32 shows the current-voltage (I-V) curves of the ZnO nanowires and VO-ZnO nanowires in dark or under UV illumination. Figure 33 shows the dynamic resistance changes of the sensors based on ZnO nanowires and VO-ZnO. Figure 34 shows the schematic illustration of the mechanism for synergistic effects of UV activation and surface VO on the RT NO₂ gas sensing performance of ZnO nanowires.

The effect of the Li doping on the physical, material, electromechanical and piezoelectric properties of the ZnO nanowires was investigated and reported by Hamid et al. [69]. The vertically aligned crystalline ZnO nanowires doped with different concentrations of the Li was grown by the low temperature hydrothermal growth technique [69]. The resulted ZnO was characterized by several techniques including the XRD, SEM, and TEM [69]. The study showed that a considerable physical, material and electromechanical property modifications of the ZnO nanowires were due to the incorporation of Li dopants [69]. In that study the Atomic Force Microscope (ATM) was used to applied controlled amount of force on the fabricated nanowires to assess their piezoelectric response [69]. The result of that study showed that more than twenty-two-fold improvement was observed in sensitivity due to the combined effect of modifications in nanowires geometry and piezoelectric properties with the addition of Li [69]. It was found that the changes in the material and electromechanical properties alone are responsible for more than seven-fold improvement in the sensitivity [69]. The impact of...
’kick-out’ diffusion mechanism of the Li in ZnO is one of the major factors responsible behind this sensitivity improvement [69]. Figure 35 shows the fabrication process flow for the nano-energy harvester/nano-sensor ZnO sensor. Figure 36 shows the SEM images of the ZnO nanowires. Figure 37 shows the variation of average nanowires length and diameter with Li doping concentration.

Figure 35. Fabrication process for ZnO nanowires sensor [69]

Figure 36. (a-e) SEM images of ZnO nanowires sensor patches with the stage tilted at 45° (f-j) Top down close-up SEM images of ZnO nanowires sensor from devices [69].

Figure 37. (a) Variation of average nanowires length and diameter with Li doping concentration (b) Variation in average density of ZnO nanowires with Li doping concentration [69]
6. Conclusion

In conclusion, the recent advances of the ZnO based nanowires based sensors was presented and discussed. ZnO has been extensively studied over the past decade. Many great efforts have been intensified for understanding the optical and electrical properties of ZnO. The ZnO based nanostructure configurations including nanowires sensors have a promising potential in gas 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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