Perspective—Doped ZnO Nanostructures Based on Ultraviolet Photosensors

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In the past decades, the variety morphologies and doping zinc oxide (ZnO) nanomaterials have attracted significant attention due to its outstanding properties for photodetectors (PDs). This perspective article provides the state of recent advancements regarding the doping of ZnO-based PDs and discusses future directions of ZnO-based optoelectronic devices. The article can provide a useful reference for those who are interested in PDs.

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This perspective article details the recent progress of ZnO nanomaterials (NMs) for photodetector (PD) applications, then compares and summarizes their sensing performance. The challenges, advantages, and future directions for building ideal ZnO-based PDs are subsequently discussed.

History and Development

The rapid progress of technology and science can provide many novel device potential applications for NMs.1 NMs generally have unique properties that are different from bulk materials when NMs critical dimensions on the nanometer scale (1–100 nm).2 For decades, researchers have turned their attention to unique properties of novel nanostructures. Among these unique properties have particularly attractive to those who are ongoing for improved performance in PDs.3 Among them, metal oxide semiconductors (MOSs) have dominated commercial PDs because of their superior performance, such as high surface area, high electron mobility, high thermal stability, and high chemical stability.4 Various MOS NMs based PDs, such as SnO2, In2O3, ZnO, WO3, Cu2O, Co3O4, NiO, and TiO2, have been explored for applications.5–12 Among them, ZnO stands out from these NMs as a promising nanomaterial for PD application owing to its various excellent sensing properties, including the detection of chemicals, gas, and biomolecules.13 Among them, ZnO PDs are the most used in environmental detection. ZnO PDs were first introduced in 2000 via Liu et al.14 They were used MOCVD to prepare the ZnO film PD on Al2O3 substrate. Over the last decades, many PDs have been prepared metal semiconductor metal (MSM) structure and p-n junction structures. These structures have their own advantages, such as MSM structures can have rectified properties when form Schottky barrier, or non-rectified properties when form ohmic contact. On the other hand, p–n junctions to increase their response speed, stable operation, and low noise.5,15 Therefore, the process design can effectively improve the overall performance of the device. In addition, ZnO can be produced in large area via low temperatures wet chemical routes, unlike other typical metal oxide materials syntheses.17

Current Status of ZnO-based Photosensors

Our environment has been influenced by the development of technology. For example, harmful emissions are depleting the ozone layer, thereby causing ultraviolet (UV) light to reach the Earth. Under the strong Sunlight, excessive exposure to UV radiation from the Sun may cause Sunburns on human bodies. Excessive UV radiation can cause wrinkles and premature aging of the skin and increase the risk of skin cancer and cataracts. Therefore, UV photosensors for health, safety, and environmental monitor have an important role.18–42 Light is absorbed when the light energy larger than the NMs bandgap excites numerous free electrons and holes at the same time, thereby increasing conductivity. An ideal PD should be sensitive in sensing region, and should possess high selectivity, high photoconductive gain, low energy consumption, high detectivity, and fast response speed. Figure 1 show the progress in ZnO-based NM PD device fabrication.

ZnO nanostructures.—ZnO NMs have many advantages, such as wide band gap (3.37 eV), large exciton binding energy (60 meV), non-toxicity, easy to obtain, and low cost.43 For the past few years, various methods to synthesize ZnO nanostructures, such as aqueous solution methods, hydrothermal method, electron-beam lithography, electrochemical deposition, and chemical vapor deposition, have attracted extensive research.44–50 Among these approaches, the hydrothermal method and aqueous solution methods are the least expensive and simplest. In addition, various morphologies of ZnO nanostructures have been developed, such as 1-D nanotubes, nanowires, nanopins, and nanorods (NRs), and 2-D nanodiscs, nanoplates, and nanosheets (NSs).51–57 The preparation method will be discussed later.

Photoluminescence (PL) of ZnO nanostructures.—The PL spectrum is a typical tool used to observe light emission from ZnO NMs after the absorption of photons. The emission band of ZnO NMs can be used to confirm the quality with UV (~380 nm)-to-visible (500 ~ 650 nm) ratio and full width at half maximum. Normally, the UV emission band of ZnO NMs is via recombination of free excitons through an exciton–exciton collision process, and visible emission band (green emission) is formed though defect from the ZnO NMs such as oxygen vacancy, zinc vacancy, interstitial zinc, and interstitial oxygen.58,59 Depending on the fabrication method or different nanostructures, the emission peak may be shifted due to quantum confinement effect.57,60,61 For example, Khaldoon et al.62 Djurisic et al.57 and Hur et al.63 reported that different ZnO nanostructures could be caused shift phenomenon of optical band gap.

Fundamentals of ZnO nanostructure PDs.—According to past reports, the surface of ZnO nanostructures adsorbs oxygen molecules can be changed conductivity of ZnO due to ZnO is n-type semiconductor. The main carriers are electrons. Thus, the negatively charged ions could be captured from free electrons, thereby giving ZnO nanostructures surfaces a large quantity of oxygen species. The adsorption reaction is as follows:82
The behavior of adsorbed oxygen molecules leads to formed transversal depletion layer on the ZnO nanostructures surface. When illuminated with UV light, PD properties are usually affected by the oxygen molecule absorption and desorption on the nanostructures surface. The photo-generated holes are driven to the surface by the depletion field and combine with the surface oxygen ions.

Future needs and prospects.—Future research on MOS-based PDs should attempt to understand the inter-relationship in all the steps of PDs, including best materials in all the steps, contact optimization, cost down, improve performance, and materials understanding. Figure 2 shows the characteristics of the ideal device, which possesses longevity, attractiveness, low price, and superior performance.

Cost reduction.—One of the main reasons for the high cost of PDs is the use of noble metal adsorption or rare Earth elements doped to enhance materials’ optical transmission properties. To date, many methods have been developed to ameliorate PD performance, such as doping group V elements N, P, As, and Sb materials for p-type of ZnO NMs. In addition, using group IB elements and group I for p-type of ZnO NMs, such as Cu, Ag, Au, Li, Na, and K atoms, have been developed. Rare Earth elements doped into ZnO NM, such as La, Eu, Dy, and Er, have also been reported. Among these, group III elements In, Al, and Ga doped ZnO NMs are useful as cost-effective doped source to enhance materials’ optical transmission properties. ZnO is a n-type nanomaterial. It can improve optical and electrical properties by doping. For example, Tin-doped indium oxide (ITO) has already been used extensively as transparent conduction oxide (TCO) film. When ZnO film was doped group III elements (Al, Ga, In), it can also increase the conductivity and good optical transmission properties. Thus, it is also potentially useful as cost effective TCOs. On the other hand, it can be changed into p-type semiconductor when ZnO is doped with group I (Cu, Ag, Au, Li, Na, K) or group V elements (N, P, As). Whether in optical, chemical, and electrical properties, it has a good improvement. However, it has still some problems which p-type ZnO NMs are unstable and difficult to reproduce because of some unknown mechanisms.

Growth methods for ZnO-based nanostructures.—The other main reason for the high cost of PDs is the growth methods of nanostructured materials. To date, several approaches have been developed to fabricate high-quality ZnO NMs, such as chemical vapor deposition, hydrothermal method, aqueous solution method, and pulsed laser deposition. Additionally, several ZnO nanostructures, such as NSs, nanorings, nanowalls, NRs, nanotubes, and nanograsses, have been developed to ameliorate PD performance. In order to develop an ideal device at low price, we suggest using a solution-based method to grow ZnO NRs because of the present advantages, such as uniform morphology, high productivity, simple and controllable process, low-temperature process, and low cost.

Hydrothermal growth method for ZnO NRs.—The growth of NRs undergoes the following chemical reactions:

\[
\frac{1}{2} O_{2(gas)} + 2e^- \rightarrow O_{ads}^2-
\]

\[
hv \rightarrow e^- + h^+
\]

\[
2h^+ + O_{ads}^2- \rightarrow O_{2(gas)}
\]

Figure 1. Progress in ZnO-based nanomaterial photodetector device fabrication.
When zinc nitrate hexahydrate and hexamethylenetetramine are added to the same de-ionized water solution and heating (~90 °C), the hexamethylenetetramine and zinc nitrate hexahydrate are decomposed into zinc ion, ammonia, and formaldehyde species in the aqueous solution. Subsequently, the hexamethylenetetramine functions as a buffer by providing stable zinc ion and hydroxide ion to constitute Zn(OH)$_2$ ion. Finally, ZnO NRs are synthesized via dehydration. Additionally, when zinc nitrate hexahydrate and hexamethylenetetramine are added to the same de-ionized water solution and heating, aluminum nitrate, gallium nitrate, and indium nitrate are added to the same solution to replace zinc ion (Zn$^{2+}$).

**Aqueous solution methods for ZnO-based NSs.**—The proposed reaction scheme is presented as follows:79

\[
\begin{align*}
Zn^{2+} + Zn(OH)^- & \rightarrow Zn(OH)_2 \\
Zn(OH)_2 + 2OH^- & \rightarrow Zn(OH)_2^{2-} \\
Zn(OH)_2^{2-} & \rightarrow ZnO + 2H_2O + 2OH^-
\end{align*}
\]

When zinc nitrate hexahydrate and sodium hydroxide are added to the same de-ionized water solution, the sodium hydroxide and zinc nitrate hexahydrate are decomposed into zinc ion, hydroxide ion, and sodium ion in the aqueous solution. Subsequently, the increased amount of sodium hydroxide further synthesizes Zn(OH)$_2$ from Zn(OH)$_2$ in the aqueous solution and Zn(OH)$_2$ as a growth unit is synthesized under the specific conditions. Finally, ZnO NSs are synthesized via dehydration. However, when zinc nitrate hexahydrate and sodium hydroxide are added to the same de-ionized water solution, the aluminum nitrate, gallium nitrate, and indium nitrate are added to the same solution to replace zinc ion (Zn$^{2+}$).

**Performance improvements.**—Contact technologies.—In the last decade, contact quality had been the focus in the research on ZnO NMs PDs. To date, many contact technologies have been developed to form a Schottky barrier or ohmic contact, such as MSM structures and p-n junction structures, which can be divided into heterojunctions and homojunctions. The chances of success of single ZnO NRs contact and multiple ZnO NRs contact based PD fabrication methods are usually low. Therefore, large quantities of test sample are needed to select a successful fabrication for ZnO-based PDs.80–88

**Multiple contact ZnO nanostructure based PDs.**—The insulating material or insulating layer must be on the substrate, then Au catalyst layer or ZnO seed layer is deposited on the substrate afterwards to define the pattern of Au catalyst layer or ZnO seed layer via etching or photolithography. After growing the ZnO nanostructures, the multiple contact of ZnO nanostructure lateral PDs can be finally manufactured.80–88 Another method is growing the ZnO nanostructures by using various methods after coating the passivation layer onto the nanostructures to lay over the surface. The passivation layer must be insulating material (such as PMMA or SOG) in order to fill the gaps between the nanostructures. Afterwards, the pattern can be defined via photolithography, then Au layer is deposited as a contact electrode; finally, the multiple contact of ZnO nanostructure lateral PDs is manufactured.

**Single contact ZnO nanostructures based PDs.**—The first step is to define the pattern of electrodes on insulating substrate. ZnO nanostructures can be grown by using various methods and then collecting them in an alcohol solution. Homogeneous disperse the ZnO nanostructures by sonication in solution, afterwards extract from solution homogeneous disperse the ZnO nanostructures in drops then dropping on insulating substrate to define the pattern of electrodes. The interface of ZnO nanostructures and electrodes to stabilize by Pt contact (used focused ion beam [FIB] equipment).89 Finally, the single contact of ZnO nanostructures PDs is manufactured. Another method of growing ZnO nanostructures is by using various methods and then collecting them in an alcohol solution, homogeneous disperse the ZnO nanostructures by sonication in solution, afterwards used to photosist (PR) spin coating to define the PR pattern on insulating substrate. Subsequently deposited electrode metal on the sample then remove the PR pattern (lift-off), finally the single contact of ZnO nanostructures PDs is manufactured.

**Figure 2.** Characteristics of the ideal photodetector and the problems it needs to solve.
Conclusions

Many evaluations have confirmed the potential of doping for enhancing ZnO PDs. Nonetheless, the application of doped ZnO PDs poses many challenges, which warrant more research. Single- and multi-contact ZnO nanostructure-based lateral PDs usually need expensive and complex fabricated processes, such as FIB, etching, and lithography, which entail high cost and pose difficulties in production. Many methods can be used to improve performance and to reduce cost. We analyzed the factors for high cost and ways to decrease them. Despite many promising advancements in doped ZnO PDs, our understanding remains limited. Efforts in the areas of materials properties and semiconductor processes is a key to build successfully high-performance PDs at low cost.

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