Photoconductive enhancement of single ZnO nanowire through localized Schottky effects

Ming-Wei Chen,1 Cheng-Ying Chen,1 Der-Hsien Lien,2 Yong Ding,2 and Jr-Hau He1,*

1Institute of Photonics and Optoelectronics, & Department of Electrical Engineering, National Taiwan University, Taipei10617, Taiwan
2School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA
*jhhe@cc.ee.ntu.edu.tw

Abstract: We demonstrated the Au nanoparticle (NP) decoration as an effective way to enhance both photocurrent and photoconductive gain of single ZnO nanowire (NW) photodetectors (PDs) through localized Schottky effects. The enhancement is caused by the enhanced space charge effect due to the existence of the localized Schottky junctions under open-circuit conditions at the NW surfaces, leading to a more pronounced electron-hole separation effect. Since the band-bending under illumination varies relatively small for an Au NP-decorated ZnO NW, the decay of gain is less prominent with increased excitation power, demonstrating the feasibility for a PD to maintain a high gain under high-power illumination.

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Due to reduced dimensionality of the active areas and high surface-to-volume ratio, nanostructure-based materials have been promising for electrical and optical applications [1–4]. ZnO nanowires (NWs) have particularly attracted extensive attentions in optical detection at the wavelengths ranging from UV and visible regions to mid-infrared region [5–7]. For Ultraviolet (UV) detectors based on ZnO NWs, the ultrahigh photoconductive gain has been achieved via the oxygen-related hole-trap states at the NW surfaces and the band-bending induced by surface electric field [8–11]. Much effort has been devoted to improve the response time and recovery time of ZnO NW photodetectors (PDs) [12–14]. It is also of interest to enhance the sensitivity of ZnO NW UV PDs. For example, it has been demonstrated that CdTe quantum dots with band gap energy of 1.5 eV are a photosensitizer to enhance the photoresponse of ZnO NWs [15]. Lao et al. have improved the photosensitivity of the ZnO NW UV PDs by functionalizing the surfaces of ZnO using the polymers that have a high absorption at the UV ranges [16]. Zhou et al. have reported that by utilizing Schottky contacts instead of Ohmic contacts, the sensitivity of ZnO NWs for UV light has been improved [13]. Doping with appropriate metal atoms has also been shown to dramatically enhance the photosensitivity of ZnO NWs as a result of avalanche photomultiplication [17].

For the surface modification, metal nanoparticles (NPs) have been used to form Schottky junctions on the NW surfaces [9,18], modify the work function [19], and induce the charge transfer [20] to achieve the better performances of NW-based devices with specific functions. In this letter, we show the feasibility of enhancing both the photocurrent and the photoconductive gain by the Au NP decoration at the surfaces of a single ZnO NW UV PD for the first time. The enhancement is due to the enhanced space charge effect via the formation...
of the localized Schottky junctions under open-circuit conditions at the NW surfaces, resulting in a more pronounced electron-hole separation effect.

ZnO NWs were prepared by heating the mixed ZnO and C powders (6.6 g: 3.3 g) in the furnace at 930 °C for 1 hour using the vapor-liquid-solid method. NWs were then transferred to Si substrates with a 200-nm-thick SiO₂ layer. NWs were adhered to the substrate by Van der waals force. Ti/Au (10nm/70nm) electrodes for contacting ZnO NWs were defined by photolithography process and deposited by an electron gun evaporator. The devices were annealed at 400 °C for 30 seconds in order to obtain Ohmic contacts. Au NPs were sputtered on the ZnO NWs using a JEOL JFC-1600 coater at low current (~10 mA) for 20 seconds. Microstructures of Au NP-decorated ZnO NW were examined using a JEOL 4000EX transmission electron microscope (TEM) operating at 400 kV with a nominal point-to-point resolution of 0.18 nm. Morphological observation was conducted with an ELIONIX-7500 electron beam lithography system operating at 50 kV with a nominal point-to-point resolution of 2 nm. Photocurrent was measured under the illumination of a He-Cd laser with a wavelength of 325nm (Model: IK3552R-G of Kimmon KOMA Co. Ind.).

A low-magnification TEM image of an NP-decorated NW is shown in Fig. 1(a). The fringes are known as thickness contours and are commonly observed in TEM specimens of NWs because NWs are cylinder-shaped. A high-magnification TEM image shows a uniform distribution of NPs with sizes of a few nm (dark spherical regions) on the NW surfaces, as shown in Fig. 1(b). The coverage rate of randomly distributed NPs is ~60%. Figure 1(c) shows a high resolution TEM (HRTEM) image of the NW without any NP, confirming that the phase of the NWs is wurtzite-structured ZnO. The measured interplanar distance of 0.26 nm corresponds to the ZnO(0002) planes, indicating that the NWs grew preferentially along the c-axis direction [21]. Figure 1(d) shows a cross-sectional HRTEM image of the NW and the NPs. The measured interplanar distances of 0.20 nm and 0.24 nm correspond to the Au(200) and Au(111) planes, respectively. By examining the interface of Au and ZnO in Fig. 1(d), there is no intermediate phase formed between Au and ZnO, indicating that there is no chemical reaction after Au NPs are sputtered on ZnO NWs.

The inset in Fig. 2(a) shows the SEM image of a single ZnO NW PD with Au-NP decoration. The diameter of the NW is ~100 nm, and the spacing between the electrodes is 2.4 μm. Photocurrent and dark current of the Au NP-decorated ZnO NW PDs are shown in Fig. 2(a). The linear behavior of I-V curves demonstrates an Ohmic contact between a single ZnO NW and the Ti/Au electrodes. The photocurrent increases with excitation power for the ZnO NW PDs with Au NP decoration. As compared with the pristine ZnO NW, a single NW with
Au NP decoration shows a significant enhancement of the photocurrent, which is more prominent at the high excitation power, as shown in Fig. 2(b)-(d). The dark current for both the pristine and the Au-NP decorated NWs remains invariable at the range of $10^{-9}$ A, indicating that Au NPs do not produce new conductive routes at the surfaces of the ZnO NWs and the SiO$_2$ substrates to contribute the dark current.

The effect of the photocurrent enhancement by Au NP decoration can be elucidated according to the band diagram of the ZnO NWs. It is known that the surface states of ZnO function as the adsorption sites. As shown in Fig. 3(a), in air ambient, oxygen molecules adsorbing at these sites act as electron acceptors by capturing free electrons from ZnO in dark ($O_2 + e^- \rightarrow O_2^-$), which redistributes the spatial density of conducting carriers and thus forms a space charge region near the surfaces [22–25]. Under illumination, photo-generated holes tend to move to the surface through the surface electric field built by the space charge effect, and thereby the possibility for electron-hole recombination is reduced due to the spatial separation effect. The lifetime of electrons is further prolonged through the oxygen desorption by the neutralization of trapped holes and charged oxygen molecules at the surfaces ($O_2^+ + h^+ \rightarrow O_2$).

The electron-hole separation effect induced by surface electric field explains the high photoconductive gain of a single ZnO NW PD [8,22]. The surface band-bending and the width of the space charge region in dark increase with the density of surface states owing to charged oxygen molecules. Figure 3(b) depicts the band-bending diagram of a single ZnO NW after Au NP decoration. Though it is difficult to estimate the actual surface barrier between ZnO NWs and Au NPs since the charge distribution for metal NPs at the nanoscale might be different from that of typical Schottky model. However, the formation of a Schottky junction induced by Au NPs on ZnO NWs still can be understood by the difference in the work function of Au (5.10 eV) and the electron affinity of ZnO (4.3–4.6 eV) [26–30]. The uniformly distributed Au NPs on NW surfaces can be treated as a lot of localized Schottky junctions under open-circuit conditions, which enhances the surface band-bending. As compared with the pristine ZnO NW PDs, the spatial electron-hole separation effect is pronounced under UV illumination and thereby the electron lifetime is prolonged for an Au NP-decorated ZnO NW PD. Accordingly, the remaining photo-generated electrons in the NW core contribute to the increase of the photocurrent. In addition, the reason that the dark current does not decrease after Au NP decoration on NW might be due to the enhanced space charge effect, which results in the more concentrated conducting carriers in the inner core of the NWs, reducing the surface scattering.
The photoconductivity enhancement is quantitatively evaluated by calculating the photoconductive gain, which is a critical parameter for evaluating the sensitivity of PDs. The photoconductive gain is defined as the number of collected electrons in a unit time divided by the number of photons absorbed by ZnO NWs in a unit time \( G = \frac{N_{\text{electron}}}{N_{\text{photon}}} \) \[8\]. The formula can be extended for simplicity as:

\[
G = \frac{\Delta I_{\text{ph}}}{q} \cdot \frac{P}{I / h\nu},
\]

where

\[
P = P \times d \times l,
\]

where \( \Delta I_{\text{ph}} \) is the difference between the photocurrent and the dark current, \( P \) is the total excitation power absorbed by the ZnO NW, \( q \) is the electron charge, \( I \) is the excitation power, \( d \) is the diameter of the ZnO NW, and \( l \) is the spacing between two electrodes. To have an insight into the enhanced space charge effect induced by Au NP decoration on the photoconduction, the photoconductive gain for the pristine and the Au-decorated ZnO NW PDs is compared in Fig. 4. Generally, the photoconductive gain decreases with the excitation power. Under illumination, photo-generated holes migrate to the surface due to the built-in local electrical field, i.e., surface band-bending. It can be expected that the local electric field will be redistributed due to the interaction between charged oxygen molecules and incoming photo-generated holes. The surface band-bending and the width of the space charge region are both decreased with the amount of photo-generated carriers, which is related to the power of UV light. This leads to the fact that the high excitation power results in the low photoconductive gain. The photoconductive gain with the excitation power can be fitted by inverse power law \[31\]:

\[
G = \Gamma^{-1},
\]

where \( k \) is the exponent. As shown in Fig. 4, the fitting exponent \( k \) for the pristine ZnO NW is 0.82 while \( k \) for the Au NP-decorated ZnO NW is 0.20, which means when Au NPs are decorated on ZnO NWs, the decay of photoconductive gain with increased power becomes less prominent. Due to the enhanced space charge effect induced by the localized Schottky junctions between Au NPs and ZnO, the variation of the width of the space charge region and the band-bending is relatively small under UV illumination, leading to the power-insensitive gain of Au NP-decorated ZnO NWs. The result demonstrated here is important for the practical PD application to maintain a high photoconductive gain under illumination with the high power. Similarly, a photoconductive gain simulation based on the volume modulation of a space charge region to explain the power-insensitive gain behaviors of thin film-based GaN PDs has been reported [31]. Further investigations are needed to understand the response and recovery time of ZnO NW PDs with Au NP decoration. It is also important to understand the
dependence of Au coverage at the NW surfaces on the photoresponse to optimize the performance of the UV PDs, which is under investigation.

![Excitation power-dependent photoconductive gain for the pristine and the Au NP-decorated ZnO NW PDs.](image)

In summary, we proposed that Au NP decoration at the NW surfaces can improve both the photocurrent and the photoconductive gain of a single ZnO NW PD. The underlying mechanism can be attributed to the fact that the pronounced electron-hole spatial separation effect via the formation of localized Schottky junctions under open-circuit conditions can be maintained under UV illumination for an Au NP-decorated ZnO NW. Besides, the enhanced space charge effect also results in an excitation power-insensitive gain, which is beneficial for a PD to maintain high gain even with the high-power excitation. This study demonstrates that Schottky metal NP decoration is effective to enhance both the photocurrent and photoconductive gain of NW PDs with high performance.

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