Bipolar photoresponse ultraviolet photodetectors based on ZnO nanowires

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Abstract
A comparative study on the photoresponse of zinc oxide nanowires in direct-current (DC) and alternating-current (AC) domains is presented. Zinc oxide ultraviolet photodetectors exhibit positive photoconductivity in DC domain which means that the resistance decreases upon illumination. However, in the frequency domain, zinc oxide nanowires exhibit a solid frequency-modulated response to the ultraviolet illumination leading to a tunable photoconductivity. It is shown that in AC domain the photoresponse of zinc oxide nanowires can be finely adjusted from the positive photoconductivity (resistance decrement) to negative photoconductivity (resistance increment) simply by tuning the driving frequency. Frequency-modulated photoresponse of zinc oxide nanostructures provides an exclusive platform for the realization of dual-response or bipolar photoresponse ultraviolet photodetectors which could be of high technological importance. The zinc oxide nanowires exhibit a responsivity of $+180 \text{ mA W}^{-1}$ to the ultraviolet illumination in the DC mode. The nanowires show an almost equal but negative responsivity in the AC domain. Practical implication of the bipolar ultraviolet photodetectors based on ZnO nanowires is presented.

1. Introduction
Ultraviolet photodetectors are used in a vast variety of applications including: chemical analysis [1, 2], military warning systems [3], solar irradiation monitoring [4], DNA sequencing [5], optoelectronic converters in photonic array beamformers [6], Bragg gratings in fiber optics in phased array antennas [7, 8], etc. Although silicon-based UV detectors benefit from the mature fabrication technology, they performance is limited to the temperatures less than 125 $^\circ\text{C}$ [9]. Moreover, since the penetration depth of UV photons into the silicon is less than few tens of nanometers, the depletion region should be formed near the surface of silicon which requires an ultra-shallow delta-like doping [10]. Additionally, Si-based ultraviolet photodetectors are very sensitive to a broad range of electromagnetic spectrum (from mid-UV up to Near-IR) which restricts their application in the presence of visible/solar irradiation. In contrary, wide bandgap semiconductors like group III nitrides and metal oxides are inherently visible/solar-blind, hence provide alternative platforms for exclusive UV detectors [2]. In the recent years, a considerable attention has been paid to the optoelectronic applications of wide bandgap metal oxide materials like zinc oxide [11–17] and titanium dioxide [18–25]. Distinctively, ZnO is one the most studied material for ultraviolet detection because of its chemical stability, low cost, strong radiation hardness, diverse forms of nanostructures, as well as a variety of simple & scalable production methods [24]. Owing to the direct bandgap of 3.3 eV, ZnO only absorbs ultraviolet photons ($\lambda < 400 \text{ nm}$) leading to a high ultraviolet-to-visible rejection ratio [25]. Moreover, zinc oxide and titanium dioxide nanocrystals are very promising for employing in the optoelectronic devices, including ultraviolet photodetectors, because they benefit from a large surface-to-volume ratio, ultrahigh sensitivity, and prolonged photo-carrier lifetime which results in the high photoconductive gain [14, 26–33].

Ohmic metal-semiconductor-metal (MSM) photoconductors [13, 15, 34], Schottky MSM photodiodes [30, 35], and inhomogeneous p-n junctions [36, 37] are the most employed configurations in the ZnO ultraviolet
detectors. It is shown that while the adsorption/desorption of oxygen molecules at the zinc oxide surface is the dominant mechanism for UV detection in the Ohmic MSM photodetectors, the barrier height modulation and interface states play the main role in the ultraviolet sensitivity of Schottky MSM photodiodes [30]. All these configurations exhibit positive photoconductivity in DC domain which means that current (resistance) increases (decreases) under ultraviolet illumination. Interestingly, depending on the driving frequency, ZnO nanowires (ZnO NWs) may exhibit both positive or negative photoconductivity in AC domain. Herein, we report the performance of zinc oxide nanowire ultraviolet photodetectors in both DC and AC modes. We show that the ZnO ultraviolet photodetector displays a tunable photoresponse in the AC mode. The strong dependence of photoconductivity on the driving frequency in AC domain is demonstrated by real-time photoresistance measurements. We propose, for the first time, a bipolar ultraviolet photodetector based on ZnO nanowires. This attribute of ZnO provides a unique platform for developing a new type of ultraviolet photodetectors with the tunable photoresponse polarity.

2. Experiment

The growth of zinc oxide nanowires is performed in an atmospheric pressure chemical vapor deposition system. A mixture of ZnO nanopowder and graphite (2:1) is used as the deposition seed. The mixture is placed in a ceramic boat and heated at the central zone of the furnace with the approximate temperature of 1100 °C. A constant flow of N₂ is introduced into the furnace as gas carrier. The nanowires were grown on the quartz substrates placed near the end of the furnace where the temperature was around 40 °C. From transmission electron microscope (TEM) analyses, the diameter of individual ZnO NWs is estimated to be 100–150 nm as is shown in figure 1(a). Selected area electron diffraction pattern of the nanowires represented in the inset of figure 1(a) matches well with the hexagonal wurtzite structure of zinc oxide. To fabricate the ultraviolet detector, Au is thermally evaporated on the quartz substrates at 10⁻⁵ mbar and then patterned into the interdigitated electrodes using standard lithography (distance between adjacent fingers = 100 μm). Then the nanowires were dispersed in methanol (10 mg in 100 ml), ultrasonicated for 20 min, and sprayed on the interdigitated substrates. An optical image and a schematic of the device configuration for photoconductivity tests.

![Figure 1](image-url)

**Figure 1.** (a) TEM image of zinc oxide nanowires. The inset shows selected area electron diffraction pattern obtained from ZnO NWs. Individual lattice vectors (A)–(C) are crystallographically identified as [1 4 - 4], [4 3 - 3], and [3 - 1 1] of the wurtzite structure of zinc oxide. (b) Optical image of the fabricated device and a schematic of the device configuration for photoconductivity tests.

3. Results and discussion

Au/ZnO/Au metal-semiconductor-metal (MSM) configuration is reported to exhibit both Ohmic [13, 30] and Schottky [35] contacts. In this study, the current-voltage characteristic of Au/ZnO/Au MSM configuration is found to be linear around zero bias which indicates Ohmic MSM contact. Current-voltage characteristic of the ZnO NWs at the two different temperatures (26 K and 296 K) is shown in figure 2(a). It is seen that at the room
At higher bias voltages, the current is at least one order of magnitude higher than the current at \( T = 26 \) K indicating thermally activation of carriers into the conduction band of ZnO NWs. Deviation from the linear behavior at higher bias voltages comes from the weakly connected nanowires which begin to contribute in current at higher bias voltages. The current-voltage characteristic of the zinc oxide nanowires in dark and upon ultraviolet illumination are compared in figure 2(b). It can be seen that under UV light the current increases at the low bias voltages. At higher voltages, the current is governed by series resistance and device does not exhibit response to the UV light. Real-time photoresponse of nanowires (in DC mode) to the ultraviolet illumination with different intensities and various illumination times are also shown in figures 2(c) and (d), respectively. These results show that ZnO exhibits positive photoconductivity in DC domain where the resistance decreases upon ultraviolet illumination owing to the generation of excess electron-hole pairs.

It is widely accepted that the photoresponse of zinc oxide nanostructures is governed by adsorption/desorption of oxygen molecules from the surface of zinc oxide [14, 15]. In darkness, the oxygen molecules in air are adsorbed onto ZnO surface. These molecules are weakly bonded to the surface via capturing the intrinsic free electrons present in the unintentionally-doped zinc oxide: \( O_2(g) + e \rightarrow O_2(ads) \). Upon illumination \( (h\nu \rightarrow e^+ + h^-) \), the excess electrons contribute in current passes through the system and hence the current increases upon illumination, while the excess photogenerated holes diffuse toward the surface where they discharge the oxygen ions resulting in the desorption of \( O_2 \) from the zinc oxide surface: \( h^+ + O_2(ads) \rightarrow O_2(g) \) [14, 15]. This neutralization process prolongs the lifetime of excess electrons by preventing recombination of excess electron-hole pairs. In this regard, the photo-response of ZnO NWs is accompanied by \( O_2 \) adsorption/desorption cycles which ultimately limits the photoresponse dynamics [15].

In the following we discuss the photoresponse of ZnO NWs in the frequency (AC) domain. Figure 3 shows the complex impedance plane of nanowires in dark and under UV illumination. It is seen that at the low driving frequencies, the resistance \( (R = \text{Re}(Z)) \) decreases upon illumination as is observed in DC domain. However, at the high driving frequencies the resistance of zinc oxide NWs increases under UV illumination. This effect is shown in the right panels of figure 3 at \( f = 60 \) kHz and \( f = 200 \) kHz which indicates a negative photoconductivity of ZnO NWs in the AC domain at the high driving frequencies. To make this effect clear, real-time AC photoresponse of zinc oxide nanowires at different driving frequencies is represented in figure 4. The frequency-modulated tunable photoresponse of ZnO NWs is apparent from figure 4 where a continuous...
Figure 3. Complex impedance plane of zinc oxide nanowires in darkness and under ultraviolet illumination (intensity = 0.4 mWcm$^{-2}$ & illumination time = 8 min). Right panels show enlarged window at $f = 50$, 60, and 200 kHz.

Figure 4. Real-time AC photoresponse of zinc oxide nanowires at various driving frequencies upon exposure to ultraviolet illumination.
evolution from the positive photoconduction (i.e. resistance decrement) at the low AC frequencies to the negative photoconduction (i.e. resistance increment) at the high AC frequencies is observed. Transition from the positive photoresponse to the negative photoresponse accomplished at around 40–50 kHz. When operating in AC domain, the contribution of negatively charged adsorbed oxygen molecules on the surface of nanowires in the current could not be ignored anymore. At the high driving frequencies, the current may passes through the surface of ZnO owing to the presence of these negatively charged oxygen molecules [29]. As mentioned above, upon illumination these molecules are desorbed from the surface by discharging via excited holes and hence the surface resistance increases under ultraviolet illumination which results in the negative photoconductivity at high AC frequencies. In this regard, the net current passing through a zinc oxide nanowire can be written as a sum of the bulk current \( I_b \) and a surface current \( I_s \): \( I_{\text{net}} = I_b + I_s \). In DC domain as well as at low driving frequencies of AC domain, the current is mainly dominated by \( I_b \). This component increases upon illumination as discussed in the preceding paragraph leading to the positive photoconductivity. On the other hand, at higher AC frequencies, the net current is carried out via the surface of nanowire (i.e. \( I_{\text{net}} \approx I_s \)). Upon photoexcitation, the excess holes diffuse toward the surface where they discharge the adsorbed oxygen molecules. Hence, the negative charge at the surface reduces under illumination, and consequently, the surface resistance increases leading to the negative photoresponse.

The tunable polarity of the photoresponse of ZnO NWs in AC domain provides a unique platform for bipolar photo-sensitive detectors based on the zinc oxide thin-films & nanostructures. Bipolar means that the polarity of changes in resistance \( \Delta R = R_{\text{light}} - R_{\text{dark}} \) may be tuned finely to be negative or positive by adjusting the driving frequency. Figure 5(a) shows the NWs’ photoresponse to UV light in DC mode, AC mode, and a combined mode i.e. switching from AC to DC. It is seen that the ZnO NWs exhibit positive photocurrent in DC mode, negative photocurrent in the AC mode, and a fast switch between the two modes alters the device photoresponse as well. This means that switching the bias condition from AC (200 kHz) to DC results in the flipping of photoresponse polarity. The switchable character of bipolar photoresponse is clear from the combined mode shown in the figure 5(a).

Figure 5(b) shows the photocurrent \( I_{\text{ph}} = I_{\text{light}} - I_{\text{dark}} \) versus incident UV intensity \( P_\text{in} \) in DC and AC domains. In DC mode (AC mode), the photocurrent changes from 11 μA (–23 μA) to 65 μA (–70 μA) as the light intensity increases from 0.25 mWcm\(^{-2}\) to 3 mWcm\(^{-2}\). In both cases, \( I_{\text{ph}} \) exhibit a fair linear dependence on the incident light intensity [38]. The dash-lines in the figure 5(b) show linear fits to the experimental data. The responsivity \( R_I = I_{\text{ph}} / P_\text{in} \) of zinc oxide NWs versus the incident light intensity in DC and AC domains is represented in figure 5(c). At the intensities higher than 200 μW, the responsivity becomes constant as is expected from the linear dependence of photocurrent shown in figure 5(b). It is seen that, the responsivity in DC mode is +180 mA W\(^{-1}\). In the AC mode, the zinc oxide NWs exhibit an approximate equal but negative responsivity. This result indicates the bipolar character of responsivity of ZnO nanowires in DC and AC domains and approves the concept of bipolar photo-sensitive devices.

To understand the frequency modulated photoconductivity of ZnO nanowires, a schematic of microscopic processes behind this effect and the corresponding energy band diagram are shown in figure 6. As mentioned previously, oxygen molecules are adsorbed on the surface of nanowires by capturing intrinsic free electrons in ZnO. Hence, there is negative charge just outside the surface of nanowire which could effectively contribute in

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**Figure 5.** (a) Real-time photoresponse of ZnO NWs under UV illumination in DC domain \((V_{DC} = 0.5 \, \text{V})\), AC domain \((f = 200 \, \text{kHz}, V_{AC} = 0.5 \, \text{V})\), and upon switching from AC to DC. (b) Photocurrent versus UV light intensity. Marks and dash-lines represent experimental data and the corresponding linear fits, respectively. (c) The responsivity of zinc oxide NWs versus incident UV intensity (lines and dash-lines are guide to eye).
the current flow through the nanowire (see figure 6(a)). In this regard, the electrical conduction can be carried out through either the bulk of nanowire (with resistance of $R_b$) or at its surface through the network of negatively charged oxygen molecules (with resistance of $R_s$). However, capturing the free electrons by outside oxygen molecules left behind a positive space-charge region in the nanowire located near its surface. This leads to an upward band bending at the surface of nanowire as shown in figure 6(b). The space-charge region is characterized by a capacitance ($C_s$) which separates the bulk and surface conduction channels. The characteristic time of this capacitance is roughly given by $\tau = \frac{R_b R_s}{R_b + R_s} C_s$. Now, the positive and negative photoconductivity can be understood as follows. In the DC domain as well as those AC modes whose driving frequency are smaller than $\tau^{-1}$, the surface capacitance works as an open-circuit component and the electrical current passes only by the bulk channel. On the other hand, at the frequencies much higher than $\tau^{-1}$, the surface capacitance is short-circuited and current passes through the surface channel. Under light, a couple of electron-hole pair is excited in the nanowire. The excess electron ($e^-$) contributes in the bulk conduction and hence the bulk resistance decreases upon illumination. Since in the DC domain the current is carried out through the bulk resistance, a positive photoconductivity is observed in this mode. The excess hole ($h^+$), on the other hand, diffuse toward the surface and discharge an oxygen molecule which leads to the desorption of that molecule. In this regard, a negative charge disappears from the surface channel and its resistance increases upon illumination. Since at higher AC frequencies the current passes mainly through the surface channel, a negative photoconductivity is observed upon illumination in the AC mode. In addition, since for each absorbed photon a unit of charge is added to bulk of nanowire and a unit of charge is reduced from the surface channel (figure 6(a)), it is expected that the net change in the resistance of the surface and bulk channels to be identical. This explains the equal responsivities obtained in DC and AC domains (figure 5(c)).

4. Conclusion

The photoresponse of zinc oxide nanowires upon ultraviolet illumination in direct current and alternating currents domains is investigated. While ZnO nanowires display a positive photoconductivity in DC domain, they may exhibit positive or negative photoconductivity in AC domain depending on driving frequency. The frequency-modulated tunable photoresponse of zinc oxide nanowires is explained based on the surface conduction channel provided by the negatively charged oxygen molecules. Tunable photoconductivity of ZnO nanowires in AC domain is demonstrated and discussed in details. It is shown that this attribute could be utilized to develop switchable bipolar ultraviolet photodetectors. The fabricated device based on the zinc oxide nanowires exhibits a constant responsivity of +180 mA W$^{-1}$ in the DC mode and an equal but negative responsivity of −180 mA W$^{-1}$ in the AC mode (200 kHz). The photodetector characterization procedure was carried out over 4 weeks and during this period we did not observe a significant decrement in the device.
performance indicating a good stability of the fabricated device. The frequency-modulated tunable photoconductivity in AC domain is an unprecedented phenomenon which is capable to open a new branch of ZnO-based ultraviolet photodetectors.

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