Giant Improvement of the Performance of ZnO Nanowire Photodetectors by Au Nanoparticles

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ZnO nanowire photodetectors with and without Au nanoparticles have been fabricated and investigated. The dark current decreases by 2 orders of magnitude and the ratio of photo current to dark current increases after covering with Au nanoparticles. Meanwhile, the decorated Au nanoparticles can drastically improve the response speed of ZnO nanowire photodetectors. A physical model based on band energy theory was developed to illustrate the origin of the improvement of performance for ZnO nanowire photodetector attached with Au. Our work suggests that rational integration of ZnO wire and metal nanoparticles is a viable approach to improving the performance of ZnO nanowire photodetectors, which may help to advance optoelectronic devices.

Introduction

Ultraviolet (UV) detectors have a wide range of applications in many areas, such as missile launching detection, flame sensing, UV radiation calibration and monitoring, chemical and biological analysis, environmental monitoring, space research, optical communications, and astronomical studies.[1] For an ideal UV photodetector, it should be very sensitive in UV region with high signal-to-noise ratio, high selectivity and high response speed. Zinc oxide (ZnO), a wide direct band gap (∼3.37 eV at room temperature) semiconductor, has been studied as a short-wavelength light-emitting material due to its large exciton binding energy of 60 meV.[2] In recent years, ZnO nanowires and nanobelts have received more and more attentions due to the potential applications as UV lasers,[3] light-emitting diodes,[4] gas sensors,[5,6] and UV photodetectors.[7−17] Because of its wide band gap, low cost, strong radiation hardness, and ease of manufacturing, ZnO are regarded as one of the most promising candidates for UV photodetectors.[18−23] In previous reports, most of the studies have been focused on the enhancement of responsivity and reset time.[10−17] For instance, Lin et al. have reported that heterogeneous Ag-ZnO nanowire photodetector exhibits a large enhancement of photocurrent (∼10^3 folds) with relatively fast and stable response speed as compared with pure ZnO nanowire device.[12] Seong et al. have found that the photocurrent was ∼5× larger after covering with ZnO nanoparticles on a single ZnO nanowire.[16] However, the loading of Ag particles in ZnO nanowire and the covering with ZnO nanoparticles can cause ∼10^2-folds and ∼2-folds increase of dark current, respectively.[12,16] The surface functionalization by polymer has been demonstrated as effective ways for improving the UV sensitivity[13] and response speed.[10,14] But most of the polymers have the strong adsorption in UV or visible region, which may reduce the quantum efficiency of the devices. Therefore, it is still a challenge to find an effective method which can decrease the dark current, increase the sensitivity and improve the response speed at one time.

The surface plasmons in nanostructured metals can couple with incident light, producing strong scattering and absorption of incident light and hence improving the performance of optoelectronic devices.[24−28] Furthermore, the nanostructured metals on the surface of semiconductor could result in the formation of a localized Schottky junction, which creates a charge depletion region in the nanowires in the vicinity of the metals. Hence, the effect of nanostructured metals is similar with that of the gate in field-effect transistor, which can reduce the dark current, enhance the sensitivity and improve the response speed. In this matter, we investigate the effect of Au nanoparticles on the performance of ZnO single nanowire photodetectors and demonstrate that the dark current decreases by 2 orders of magnitude after covering with Au nanoparticles. Furthermore, giant enhancements of photoresponse and response speed have been also realized by Au nanoparticles at the same time. A physical model based on band energy theory was developed to illustrate the origin of the improvement of performance for ZnO nanowire photodetector attached with Au.

Experimental Details

The ZnO nanowires used in this study were synthesized in a horizontal tube furnace by a chemical vapor deposition method on sapphire substrate. Gold films with the nominal thickness of 3 nm were deposited on the substrates before the growth of ZnO nanowires using as catalyst. A mixture of highly pure (99.999%) ZnO powder and (99.999%) graphite powder with a weight ratio of 1:1 ZnO/C was used as the source. The growth temperature and pressure were 935 °C and 9.0 × 10^2 Pa, respectively. Highly pure argon mixed with 3% oxygen was used as the carrying gas. After growth, the system was cooled to room temperature. To fabricate ZnO single nanowire photodetector, the ZnO nanowires were first dispersed into the ethanol solution. Then the nanowires solution was divided into two parts (solution A and solution B) and Au nanoparticles (diameter = 30 nm) was dissolved into solution B to form Au-absorbed ZnO nanowires. After that, ZnO nanowires with and

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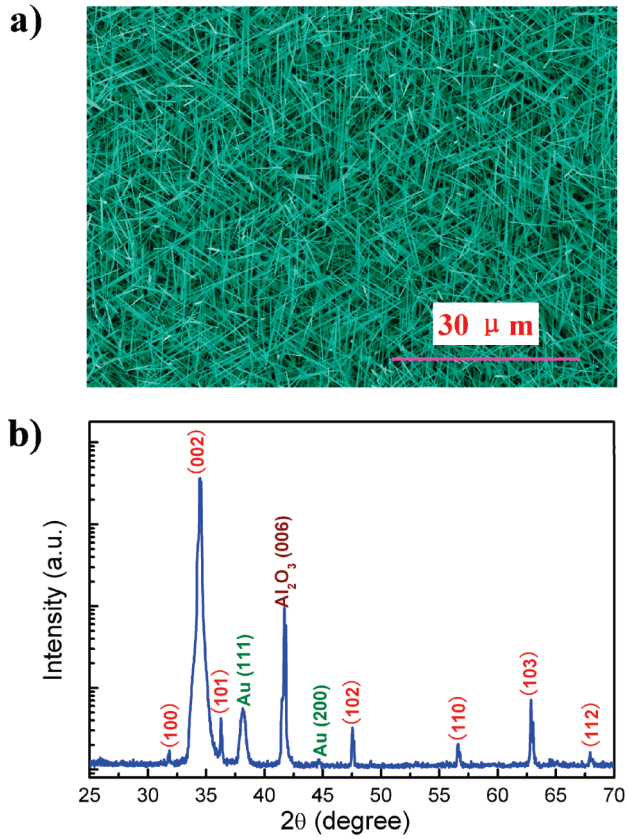

Figure 1. SEM image (a) and XRD pattern (b) of as-grown ZnO nanowires on sapphire substrate.

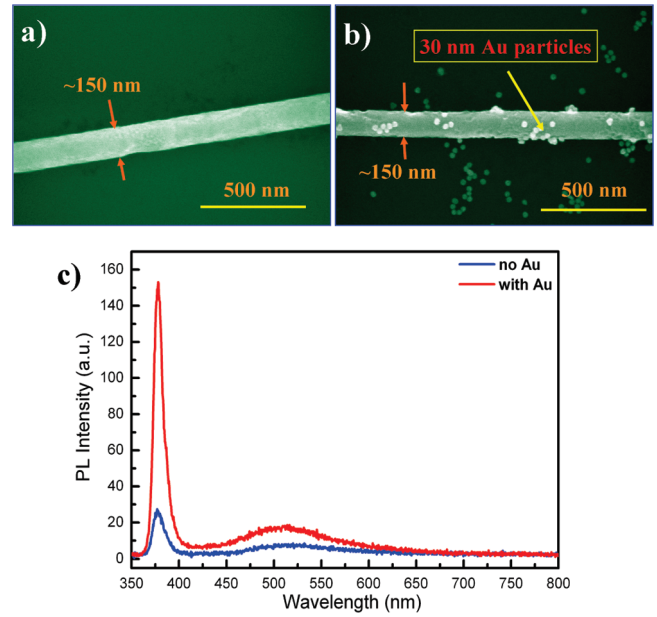

Figure 2. (a) SEM image of ZnO nanowire. (b) SEM image of ZnO nanowire with Au nanoparticles. (c) PL spectra of ZnO nanowires with and without Au nanoparticles at room temperature.

without Au nanoparticles were dispersed on the SiO_2 (100 nm)/Si templates, followed by drying with a lamp to remove the organic solvent. The Au electrodes with a thickness of 100 nm were prepared by e-beam lithography. The morphology and the structural quality of ZnO nanowires were characterized and investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The PL measurements were carried out at room temperature using a He−Cd laser (325 nm line). The current−voltage ($I-V$) characteristics of an individual ZnO nanowire-based photodetctor were measured in air using an Advantest picoammeter R8340A and a dc voltage source R6144. The time responses of devices to light irradiation were measured by a current meter after shutting the UV light. A xenon lamp (500 W) was selected as UV light source.

Results and Discussion

The SEM image of as-grown ZnO nanowires is shown in Figure 1a. The as-grown nanowires in our case are disordered and have similar size with an average diameter of about 150 nm and a length of about 10 μm. Figure 1b shows a typical XRD pattern of the as-grown ZnO nanowires on sapphire substrate. ZnO nanowires can be indexed as the wurtzite hexagonal structure. Meanwhile, Au (111) and (200) peaks can be also observed which should come from the catalyst. No other phases such as Zn can be found in our samples.

Figure 2a,b are the high magnification SEM images of ZnO nanowires dispersed on SiO_2/Si template with and without Au nanoparticles, respectively. It can be found that two ZnO nanowires have the same diameters (~150 nm). Furthermore, as shown in Figure 2b, Au nanoparticles are dispersed on the surface of ZnO nanowire randomly and do not cover the whole surface of the nanowire. In order to investigate the effect of Au nanoparticles on the optical properties of ZnO nanowires, the micro PL spectra measurements have been carried out at room temperature on the aforementioned two ZnO nanowires. Figure 2c shows the micro PL spectrum of ZnO single nanowires with and without Au nanoparticles excited by a CW He−Cd laser. It consists of a strong, excitonic UV emission and a relatively weak visible emission due to oxygen vacancy for both two samples.[29] A giant enhancement of UV emission (~7 folds) and a small enhancement of visible emission (~1.5 folds) were observed by the decorated Au nanoparticles. Several mechanisms can be responsible for this emission enhancement. Because Au nanoparticles partly covered the ZnO surface and the contact region between ZnO and Au was very small, surface-modification effect should be neglected in our case. According to our previous report,[30] the enhancement by Au nanoparticles can be attributed to the interaction between the spontaneous recombination in ZnO and localized surface plasmons (LSPs) arising from Au nanoparticles. Additionally, the increase of light absorption due to the scattering by Au nanoparticles is another reason for this enhancement.[24] As for the difference in enhancement ratios for UV and visible emissions, it should be associated with energy of LSPs in Au nanoparticles which is sensitive to the morphology of metals.

Schematics of ZnO nanowire-based photodetectors with and without Au nanoparticles and a representative SEM image of this device are shown in Figure 3a−c, respectively. The Au electrodes are 100 nm thick and the distance between two electrodes is 2 μm. Figure 3d shows typical $I-V$ characteristics of ZnO nanowires with and without Au nanoparticles both in dark and under UV illumination (λ = 350 nm, Power density = 1.3 mW/cm^2). The $I-V$ curves in dark for two devices are nolinear, which indicates that Au electrodes and ZnO nanowires are typical Schottky contacts. At 1 V bias, the dark currents are 0.13 pA and 9.7 pA for the devices with and without Au nanoparticles, respectively. The equivalent circuit for the devices was shown in the inset of Figure 3d. The schematic structure of the device can be considered as a single ZnO nanowire connected with two back-to-back Schottky barriers. When the devices are illuminated by 350 nm UV light, the currents

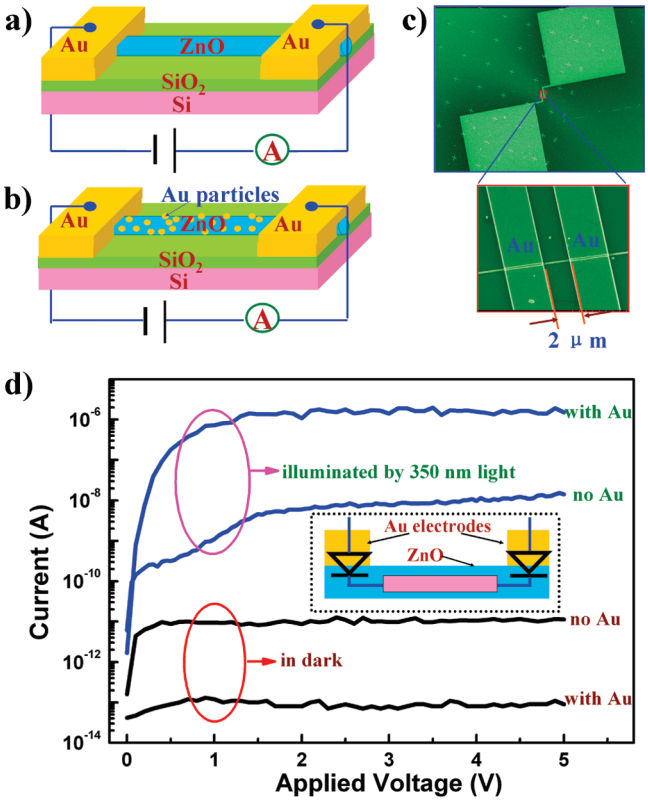

Figure 3. Schematic of ZnO nanowire photodetectors without (a) and with (b) Au nanoparticles. (c) SEM image of the device. (d) $I-V$ characteristics of ZnO nanowire photodetectors both in dark and under 350 nm UV light illumination. The inset of Figure 3d is the equivalent circuit for the devices.

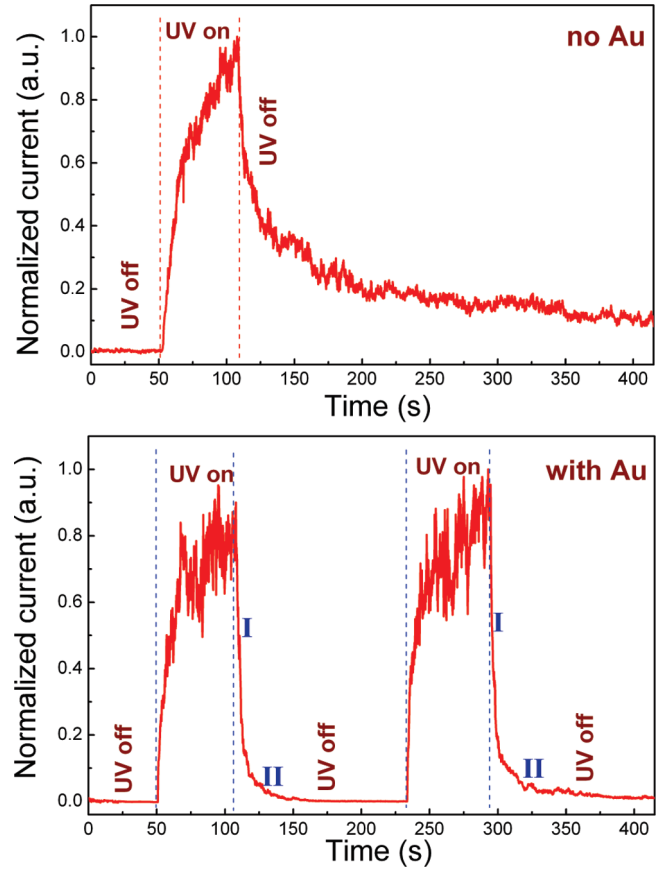

Figure 4. Photoresponse behavior of ZnO nanowire photodetectors without (a) and with (b) Au nanoparticles.

increase largely due to the photon energy (350 nm, 3.54 eV) is larger than E_g of ZnO (3.4 eV) and they can produce electron−hole pair, thereby changing the electrical conductivity of ZnO. The UV photoresponse should origin from two parts: the nanowire itself and the Schottky contact between Au electrode and ZnO just as shown in the inset of Figure 3d. The ratio of photo current to dark current of bare ZnO photodetector is around 10^3. As for the device with Au naoparticles, this value can be increased as large as 5×10^6. These results indicated that covering with Au nanoparticles on the surface of devices can decrease the dark current and increase the photocurrent. In other words, signal-to-noise ratio and responsivity of ZnO nanowires-based photodetectors can be increased largely by covering with Au nanoparticles.

The normalized time-dependent photocurrents for ZnO nanowire photodetectors with and without Au nanoparticles under fixed bias of 1 V are shown in Figure 4. As shown in Figure 4a, the current of bare ZnO nanowire device increased quickly by 350 nm UV light illumination and was not saturated after 50 s continuous illumination. After turning off the UV light, the current decreased to the 20% of its maximum in 100 s and kept this value for a long time. As for the device with Au nanoparticles, the speed of the current increase was similar with that of bare ZnO device. When the UV light was turned off, the current decay starts with a fast decay component (see "I" in Figure 4b). After that, a much slow current decay process (see "II" in Figure 4b) lasts for a long time (it should be noted that the current in region "II" was 10× larger than its initial value) and this trend is similar with that of bare ZnO device. By comparing Figure 4, parts a and b, it can be found that the rise time (defined as the time for the current to rise to 90% of the peak value) are around 40 and 25 s for the device without and with Au nanoparticles, respectively. As for the decay time (defined as the time for the current to decay to 10% of the peak value), it decreases from ∼300 s to ∼10 s after covering with Au. These results indicate that the reset time of ZnO nanowire photodetector can be decreased largely by Au nanoparticles.

The $I-V$ characters and time-dependent photocurrent measurements provide that the decorated Au-nanoparticles on the surface of ZnO nanowire can remarkably improve the performance of ZnO single nanowire photodetector. In order to well understanding the mechanisms of these performance enhancements, a model based on energy band theory was proposed in this letter as shown in figure 5. Schematics of the ZnO nanowires (with and without Au nanoparticles) energy band diagrams in dark and under illumination are displayed in figures 5a and 5b, respectively. In the dark, oxygen molecules are adsorbed on the surface of ZnO nanowires and capture the free electrons in the n-type ZnO semiconductor [$O_2 + e \rightarrow O_2^-$].[9,31,32] Thereby, a depletion layer with low conductivity is created near the surface. After covering with Au nanoparticles, the surface states and the adsorption of oxygen molecules do not change due to that Au nanoparticles do not cover the whole surface of the nanowire and the contact region between Au and ZnO is very small. Additionally, since the work function of Au ($\varphi_{Au} = 5.1$ eV) is larger than that of ZnO ($\varphi_{ZnO} = 4.1$ eV),[15] electrons will flow from ZnO to Au and a Schottky barrier is formed at the interface, where Au nanoparticle and ZnO have the same Fermi energy level (E_F). The negatively charged Au nanoparticle depletes the carriers near the surface of ZnO nanowires. Since the width of depletion layer is related to barrier height, depletion region near the Au nanoparticle is larger than that at defect and adsorbed oxygen site. The formation of the large depletion

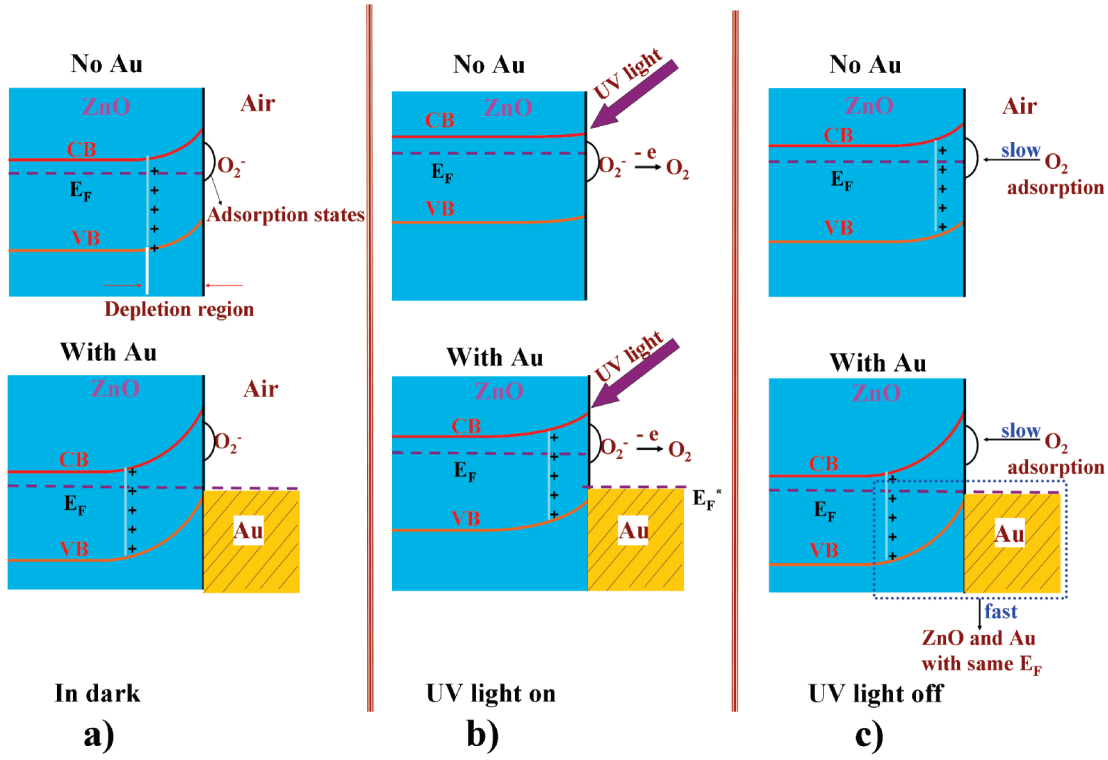

Figure 5. The energy band diagram near the surface of ZnO and Au in dark (a), under UV light (b) and after turning off the UV light (c). VB and CB are the valence and conduction band, respectively. Oxygen molecules adsorbed at the nanowire surface can capture the free electron present in the n-type semiconductor forming a low-conductivity depletion layer near the surface. The high work function Au metal forms a localized Schottky barrier in the vicinity of Au-nanoparticles, which will increase the height and the width of space chare region.

region is the main reason for the decrease in the dark current after covering with Au nanoparticles. Under UV illumination (see Figure 5b), electro-hole pairs are generated in ZnO nanowires [$h\nu \rightarrow h^+ + e$]. The photogenerated holes migrate to the ZnO nanowire surface and then discharge the negatively charged oxygen ions by surface electron−hole recombination [$h^+ + O_2^- \rightarrow O_2$]. These photogenerated electrons increase the conductivity of the ZnO nanowires. As for the Au nanoparticles-adsorbed ZnO nanowires, the light absorption efficiency can be increased by particles-induced light scattering.[24] Hence, the quantity of photogenerated electron−hole pairs increases in ZnO nanowires. Additionally, generated holes migrate to the Au nanoparticle due to the interactive Coulomb force. Some of the holes are trapped at the Au−ZnO interface and some of the holes pass through the Schottky barrier at the interface. The holes passing through the barrier make electron−hole recombination. The screening and the decrease of the negative charge lead to the difference in the Fermi level as schematically shown in the bottom of Figure 5 b). These processes decrease the width of the depletion layer. Additionally, the Schottky barrier at the Au nanoparticles−ZnO nanowire interface can exhibit hole-trapping that allows more electrons can be collected by electrodes. Therefore, the particle-induced scattering and Schottky contacts (between Au nanoparticles and ZnO nanowire) can be responsible for the large enhancement of photoresponsibility of ZnO nanowire-based sensor. In addition, the effect of LSPs arising from Au nanoparticles may be another reason. After turning off the UV light (shown in figure 5c), the electron−holes recombine, resulting in a conductance decrease. Meanwhile, oxygen molecules are readsorbed on the surface of ZnO nanowires, creating a depletion layer with low conductivity. The oxygen readsorption process is very slow and it should take a long time to recover the initial state (before UV illumination),[33] so the photocurrent decay time after turning off the UV light is very long just as shown in Figure 4a. For the device with Au nanoparticles, besides the electron−holes recombination, two main mechanisms can be responsible for the photocurrent decay process: oxygen readsorption and establishing a uniform E_F between Au nanoparticles and ZnO nanowire. Establishing a uniform E_F and forming a depletion layer on the surface of ZnO nanowire should be a very fast process. The large depletion layer is the obstruction of electron flowing and lead to the large decrease of photocurrent, as shown in region "I" in Figure 4b. The slow decay in region "II" (see Figure 4b) should be caused by oxygen readsorption process, which is the same with bare ZnO nanowire device.

Conclusions

We have demonstrated that Au nanoparticles on the surface of ZnO nanowires can improve the performance of photodetectors. The dark current decreases by 2 orders of magnitude after covering with Au nanoparticcles due to the Au nanoparticles can further deplete the carriers near the surface of ZnO nanowires and increase the width of depletion layer. Au nanoparticle-induced light scattering can increase the light absorption efficiency, thereby increasing the ratio of photo current to dark current from 10^3 to 5×10^6. The processes related to holes near the nanoparticle and the effect of LSPs also attribute to this enhancement. Additionally, the decay time (defined as the time for the current to decay to 10% of the peak value) of the device has been largely reduced from ~300 s to ~10 s by Au nanoparticles. The origin for this phenomenon with Au may be related to the quick process for establishing a uniform E_F between Au nanoparticles and ZnO nanowire.

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