

High-performance UV detector made of ultra-long ZnO bridging nanowires

Yanbo Li, Florent Della Valle, Mathieu Simonnet, Ichiro Yamada and Jean-Jacques Delaunay¹

Department of Engineering Synthesis, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

E-mail: jean@mech.t.u-tokyo.ac.jp

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Abstract

A nanowatt UV photoconductive detector made up of ultra-long ($\sim 100 \mu\text{m}$) ZnO bridging nanowires has been fabricated by a single-step chemical vapor deposition (CVD) process. The electrodes, forming comb-shaped thick ZnO layers, and the sensing elements, consisting of ZnO nanowires bridging the electrodes, were fabricated simultaneously in a single-step CVD process. The device showed drastic changes (10 – 10^5 times) in current under a wide range of UV irradiances (10^{-8} – $10^{-2} \text{ W cm}^{-2}$). Moreover, the detector exhibited fast response (rise and decay times of the order of 1 s) to UV illumination in air, but no response to visible light ($h\nu < 3.2 \text{ eV}$). Our approach provides a simple and cost-effective way to fabricate high-performance ‘visible-blind’ UV detectors.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The potential of ZnO to develop UV optoelectronics is one of the major motivational factors behind the considerable research interest in this wide bandgap ($E_g \sim 3.3 \text{ eV}$) material [1, 2]. In recent years, UV detectors based on ZnO thin films [3–5], nanowires [6–9], nanorods [10], tetrapods [11], nanobelts [12] and microtubes [13] have been developed. Among them, ZnO nanowires are especially attractive because of their ease of fabrication and unique properties such as high surface-to-volume ratio and carrier confinement in two dimensions that could improve device performance. However, the integration of the nanowires into working devices still remains a challenge. In the conventional ‘pick and place’ method, nanowires are collected from substrates on which they were initially grown and, then, are dispersed randomly on an insulating substrate after being diluted in a solution. Sophisticated techniques such as photolithography [7], electron beam lithography [8] or focused ion beam [14] are required to make metallic contacts to the nanowires. Although this method provides a means to study fundamental properties of single nanowires, it is complicated, time-consuming and uneconomic, thus hampering the development of practical applications.

Recently, devices based on bridging nanowires have been realized and show promising properties [15–21]. In this new technique, a trench is usually etched into a single-crystal substrate and nanowires are grown across the trench from one electrode to the other by a self-organized growth process. Since the electrodes are made prior to the nanowire growth, nanowire deterioration is minimized. Also the nanowire integration process is much more efficient in comparison to the ‘pick and place’ method. However, in order to achieve epitaxial nanowire growth and ohmic contacts between the trench walls and the nanowires, expensive single-crystal substrates with the same material as that of the nanowires are used to make the trench. For instance, GaAs [15], silicon on insulator (SOI) [16, 21] and GaN on sapphire [19] wafers were used to microfabricate trenches and grow GaAs, Si and GaN bridging nanowires, respectively. In contrast to the homogeneously bridged nanowires, heterogeneously grown bridging nanowires do not show ohmic contact properties, as was observed for ZnO bridging nanowires grown across Si trenches [17, 18, 20]. Besides, microfabrication techniques such as photolithography, lift-off and reactive ion-etching are needed to fabricate the trenches, making this method economically unfavorable for practical applications.

In this paper, we demonstrate a ZnO bridging nanowire photoconductive UV detector fabricated by a single-step

¹ Author to whom any correspondence should be addressed.

chemical vapor deposition (CVD) method without resorting to any microfabrication process. Au catalyst is patterned on a quartz glass substrate using a comb-shaped mask and then ZnO is grown on the patterned substrate by CVD. A thick ZnO layer forms on the Au-patterned areas and this layer serves as native electrodes. Ultra-long ($\sim 100 \mu\text{m}$) ZnO nanowires are grown across the gap between the ZnO electrodes, and the nanowires serve as the sensing elements of the detector. The device is able to detect UV light at irradiance down to tens of nanowatts per square centimeter. Further, the device shows high sensitivity to a wide range of UV irradiance levels: the current increased by one order of magnitude at 50 nW cm^{-2} and by five orders at 48 mW cm^{-2} . In addition, the time-dependent photoresponse measurements and the spectral photoresponse measurements show that the device has a very fast response to UV light, but has no response to light with energy lower than the bandgap energy of ZnO.

2. Experimental details

The ZnO bridging nanowire UV detector was fabricated by a CVD process in a horizontal tube furnace at 1000°C . A chemically etched metal mask with a comb-like shape was used to pattern a quartz glass substrate with $\sim 2 \text{ nm}$ Au discontinuous layer which serves as a catalyst. The number of comb fingers was 25, their length was 5 mm and the width of the fingers and the gap between them were both $100 \mu\text{m}$. A powder mixture of 0.4 g ZnO (Koch Chemicals, 99.999% purity) and 0.2 g graphite (NewMet Koch, 99.999% purity) was charged in an alumina boat located at the center of the furnace. The substrate was placed $4\text{--}6 \text{ cm}$ away from the source and downstream of the carrier gases. Argon and oxygen with a ratio of 3:2 were used as the carrier gases at a working pressure of $\sim 30 \text{ Torr}$. The temperature was kept at 1000°C for 30 min and then cooled down naturally to room temperature. Scanning electron microscope (SEM) images of the sample were taken with a Hitachi S3000N.

For electrical measurements, copper wires were fixed by indium granules on both pads of the combs. $I\text{--}V$ characteristics were measured by sweeping the bias voltage from -5 to 5 V using a picoammeter (Keithley, 6487) or a source meter (Keithley, 2400) connected with a GPIB controller to a computer. Before the dark $I\text{--}V$ measurement, the sample was kept in the dark for more than 24 h to stabilize the dark current. The background irradiance was less than 1 nW cm^{-2} . For $I\text{--}V$ measurements under UV illumination, a mercury arc lamp was used as the light source and an excitation filter centered at 350 nm ($\pm 30 \text{ nm}$) was put in front of it. The UV irradiance was varied by using different combinations of neutral density filters and measured using an optical power meter (Ophir PD300-UV). The time-resolved measurements used the same experimental set-up as that of the $I\text{--}V$ measurements, except for the use of a mechanical shutter for turning the UV light on and off. The cathodoluminescence (CL) spectrum of the ZnO nanowires bridging the gap between the two electrodes was measured by spatially resolved CL spectroscopy (Horiba, MP-32M, integrated to a field-emission SEM, JEOL JSM-7000F).

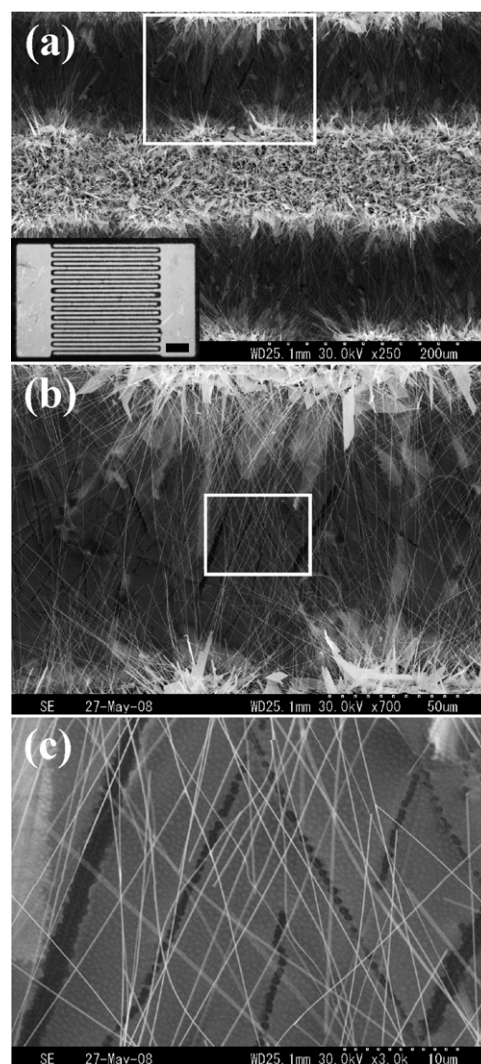


Figure 1. (a) SEM image of the comb fingers and gaps between them. The bottom-left inset shows an optical microscopy image of the fabricated device; the scale bar is 1 mm . (b) A close-up of the area outlined in white in (a). (c) Magnified view of ZnO nanowires of the area outlined in white in (b).

3. Results and discussion

Figure 1 shows typical SEM images of the ZnO bridging nanowire UV detector. ZnO was found to grow selectively on top of the Au layer and form comb-shaped ZnO thick layers. As displayed in the inset of figure 1(a), only the Au-patterned areas, i.e. the pads and fingers of the combs, were found to be covered with a thick white layer. SEM observation revealed that this white layer was composed of ZnO nanowires and nanosheets (figure 1(a)). The selective growth of ZnO on the Au-patterned areas is made possible for two major reasons: (1) Au atoms have a strong binding affinity to ZnO [22] and (2) the quartz glass substrate has a very low surface energy so that nucleation events do not take place without the presence of Au [23]. It was also found that the gaps between the comb fingers were bridged by many ultra-long ($\sim 100 \mu\text{m}$) ZnO nanowires that can be seen in figure 1(b). The formation of nanobridges is achieved

through lateral growth of ZnO nanowires at the thick layer edges, where the nanowires grow towards the neighboring fingers. When the nanowires grow long enough, they reach the ZnO thick layers grown on the neighboring fingers and form bridges. The unusually high partial pressure of oxygen we used in the CVD process is thought to facilitate the growth of ultra-long nanowires. Figure 1(c) shows that the nanowires have a uniform diameter of ~ 100 nm and some of them are interconnected. The total number of nanowires across the gap was estimated to be in the range of 10^4 – 10^5 . Transmission electron microscopy results (not shown) reveal that the nanowires are single crystalline and grow along the [0001] direction. The fingers and the pads of the combs that have much lower resistance than the bridging nanowires serve as native electrodes, while the bridging nanowires are the sensing elements of the photodetector. The fact that the two interlaced combs are not connected directly by the thick layers but by many high-aspect-ratio nanowires is thought to be responsible for the high performance in UV detection of the device. Without resorting to any lithographic process to make electrodes, the fabrication of our device enjoys an apparent advantage in terms of its great simplicity over the ‘pick and place’ method, in which many sequential fabrication steps are required to make the metal electrodes [7, 8]. More importantly, our approach avoids contamination of the nanowire surface during the lithographic processes. Since the surface condition of the nanowires is crucial to UV sensing properties, this may also benefit the device performance. Moreover, most of the nanowires are lying above the substrate, rendering their surfaces fully exposed to ambient atmosphere. This contrasts with photodetectors fabricated by lithography, for which nanowires are in contact with the substrates, so that their exposed surface is reduced and their electrical properties may be affected.

The results of I – V characteristics of the ZnO bridging nanowire photodetector under various UV irradiances are summarized in figure 2. The curves in figure 2(a) are nearly linear, indicating good connection of the ZnO nanowires between the fingers and the ohmic contact nature of the In/ZnO contacts under UV illumination. As shown in figure 2(b), significant increase in current has been observed. Compared to dark current, the current increases by more than one order at an irradiance as low as 50 nW cm $^{-2}$, and by five orders at 48 mW cm $^{-2}$. Despite the simplicity of our fabrication method, the responsivity of the bridging-nanowire-based UV detector is comparable to that of the ZnO single-nanowire photodetector for high irradiances, and is even better for low values of irradiance [8]. These results are evidence for the high sensitivity of our device to UV light and for the ability to detect irradiance down to $\sim 10^{-8}$ W cm $^{-2}$.

The photoresponse of ZnO is generally governed by adsorption and desorption of oxygen molecules on the surface. Oxygen molecules adsorbed on the surface of ZnO nanowires not only decrease the carrier density in the nanowires by trapping free electrons ($O_2(g) + e^- \rightarrow O_2^-(ad)$) of the n -type semiconductor, but also decrease the mobility of the remaining carriers by creating a depletion layer near the surface. This process also leads to upward band bending near

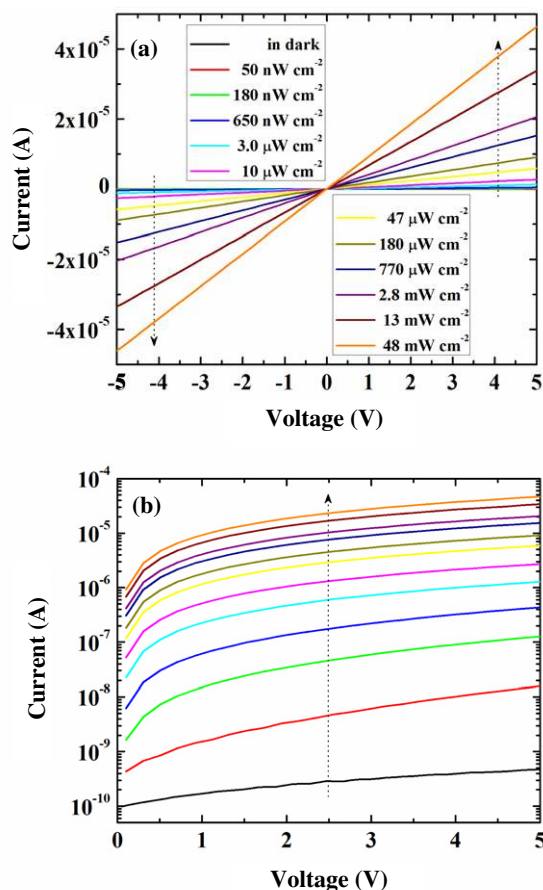


Figure 2. I – V characteristics of the ZnO bridging nanowire UV detector under different irradiances on (a) a linear scale and (b) a logarithmic scale. Insets in (a) give the irradiance values under which the curves were taken. The UV irradiance of the curves increases in the direction of the arrows.

the surface [6]. Due to the large surface-to-volume ratio, the adsorption of O_2 significantly decreases the conductivity of the nanowires, as indicated by the high value of the dark resistance (> 10 G Ω) observed in our experiments. When exposed to photons with energy higher than E_g , electron–hole pairs are generated ($h\nu \rightarrow e^- + h^+$). Holes migrate to the surface along the potential slope created by the band bending and recombine with the O_2 -trapped electrons, thus releasing O_2^- from the surface ($O_2^-(ad) + h^+ \rightarrow O_2(g)$). The remaining unpaired electrons become the major carriers in the nanowire and contribute to the current unless they are trapped again by reabsorbed O_2 molecules on the surface. The photogenerated electron–hole pairs enhance the conductivity by increasing the carrier numbers and lowering the barrier height at the same time.

The electron–hole pairs generated by absorbed photons with energy higher than the bandgap energy of semiconductors are the essence of the rise in conductivity upon illumination. Therefore, with a bandgap energy of ~ 3.3 eV at room temperature, ZnO is a promising candidate for ‘visible-blind’ photodetection. The result of spatially resolved cathodoluminescence measurement of the ZnO nanowires bridging the gap between the electrodes is shown in figure 3 (right axis). The strong UV peak at 3.28 eV and the

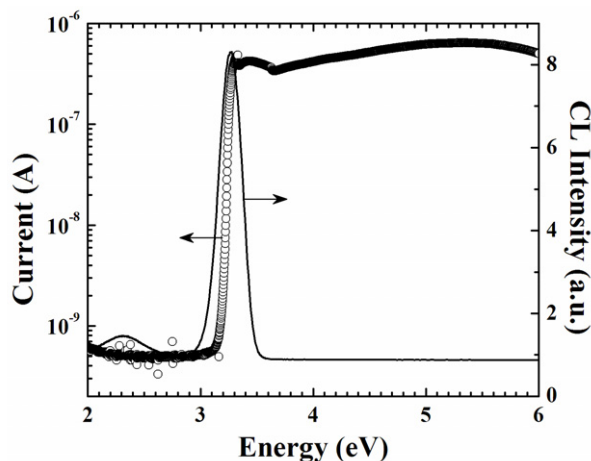


Figure 3. Spectral photoresponse (left axis and open circles) of the ZnO bridging nanowire UV detector taken with an applied voltage of 5 V, together with a room-temperature CL spectrum (right axis and solid line) of the same sample.

weak green peak at ~ 2.3 eV in the CL spectrum suggest that the ZnO nanowires have good crystallinity and low defect density [24, 25], which is crucial for achieving good performance in optoelectronic device. The spectral photoresponse (left axis of figure 3) of the same sample shows that it is insensitive to photons with energy below 3.2 eV. The current exhibits an abrupt increase from 3.2 to 3.3 eV, which matches the near-band-edge peak position of the CL spectrum, i.e. E_g of ZnO nanowires. Above 3.3 eV, the current is almost constant, except for small changes caused by variations in the irradiance ($\sim 1 \mu\text{W cm}^{-2}$) of the illumination source.

The time-dependent measurements of photoresponse were employed to study the rise and decay time upon switching UV light on and off. As shown in figure 4, both rise and decay are fast, featuring a square response for most obtained curves. For example, under a typical irradiance of $10 \mu\text{W cm}^{-2}$, the rise time (defined as the time for the current to rise to 90% of the peak value) is 0.7 s and the decay time (defined as the time for the current to decay to 10% of the peak value) is 1.4 s. The ultra-long nanowires bridging the fingers are essential to achieve fast response, as evidenced by the following observations: uniform layers that have the same structure as the thick layers of the comb fingers and pads exhibit slow responses under the same measurement conditions; failed devices that have comb fingers connected by large ZnO microstructures also exhibit slow responses. It is also observed that the rise time decreases when the irradiance is increased. Moreover, the current rise process has two phases with different response times, a phenomenon which becomes more obvious at high irradiance (see the curves in figure 4 for irradiance larger than $3 \mu\text{W cm}^{-2}$). Indeed, the current increases rapidly to a certain level upon switching on UV light and then increases gradually until the end of the UV exposure, indicating that there must be two different mechanisms behind the two phases. The fast rise could be attributed to the solid-state process in which electron-hole pairs are generated instantaneously by UV light and increase the carrier density

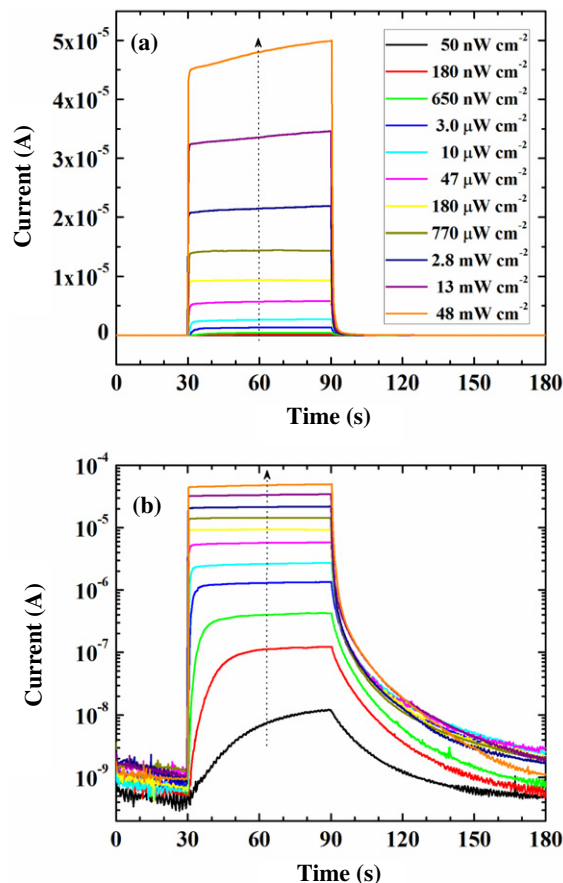


Figure 4. Time-dependent measurements of photoresponse by switching on (at 30 s) and off (at 90 s) UV light with different irradiances represented on (a) a linear scale and (b) a logarithmic scale. Inset in (a) gives the irradiance values of UV illumination. The UV irradiance of the curves increases in the direction of the arrows.

in the nanowires. The slow rise is thought to be governed by surface effects such as gas adsorption and desorption. Similarly, current decay also follows a fast and a slow process which relate to the recombination of photogenerated electron-hole pairs (solid-state process) and gas reabsorption (surface effects), respectively.

The reproducibility of the device was also tested by repeatedly switching UV light on and off for the same time intervals. As shown in figure 5, very good reproducibility is demonstrated by the observed nearly identical current rises and decays over six cycles. This result also indicates that the UV sensing mechanism involves some reversible interactions between the ZnO nanowires, ambient gases and UV light. Furthermore, figure 5 points to two interesting characteristics. First, the current decreases gradually during UV illumination under relative humidity (RH) of 73%, unlike the gradual increase observed in figure 4 for a lower RH of $\sim 50\%$. Second, the current recovers faster to the dark level under high RH. These phenomena indicate that RH, or more specifically water molecules, has a great impact on UV sensing results. The effect of water on the photoresponse of ZnO bridging nanowires is being systematically investigated and the results will be presented in future publications.

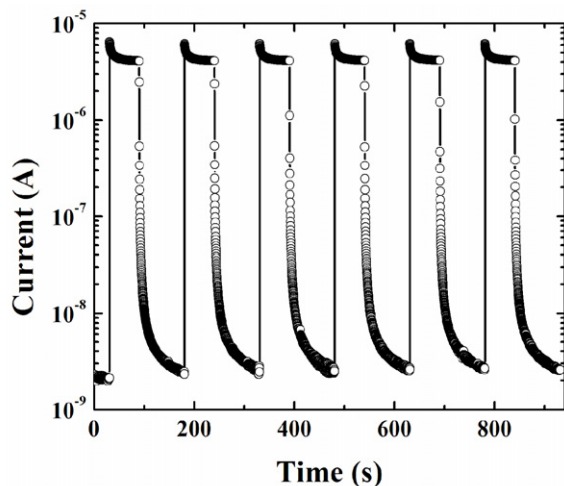


Figure 5. Photoresponse of the ZnO bridging nanowire UV detector with UV light on (for 60 s) and off (for 90 s) over six cycles. Bias voltage was 5 V and irradiance was 0.76 mW cm^{-2} .

4. Conclusions

We proposed a method to fabricate ZnO bridging nanowire structure exhibiting high performance in UV detection. This method consists in one single-step CVD process, in which the electrodes and sensing elements are fabricated at the same time. The electrodes are formed by the thick ZnO layers covering the Au-catalyst-patterned areas on the substrate, and the sensing elements consist of the ultra-long ZnO nanowires bridging the electrodes. The fabricated nanobridge device achieve both high sensitivity and fast response to UV illumination in ambient air. The proposed method is cost effective and amenable to large scale production. Moreover, this method can be applied to other metal oxide materials to fabricate similar bridging nanostructures, which are expected to show high performance in photodetection and gas sensing.

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