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p-Cu₂O-shell/n-TiO₂-nanowire-core heterostructure photodiodes

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Abstract

This study reports the deposition of cuprous oxide [Cu₂O] onto titanium dioxide [TiO₂] nanowires [NWs] prepared on TiO₂/glass templates. The average length and average diameter of these thermally oxidized and evaporated TiO₂ NWs are 0.1 to 0.4 μm and 30 to 100 nm, respectively. The deposited Cu₂O fills gaps between the TiO₂ NWs with good step coverage to form nanoshells surrounding the TiO₂ cores. The p-Cu₂O/n-TiO₂ NW heterostructure exhibits a rectifying behavior with a sharp turn-on at approximately 0.9 V. Furthermore, the fabricated p-Cu₂O-shell/n-TiO₂-nanowire-core photodiodes exhibit reasonably large photocurrent-to-dark-current contrast ratios and fast responses.

Introduction

UV photodetectors are important devices that have a range of commercial, research, and military applications. They can be used for space communication, ozone layer monitoring, and flame detection [1]. In recent years, high-performance GaN-based (including AlGaIn and AlInN) [2-5], ZnO-based [6], and ZnSe-based [7] photodetectors have all been demonstrated. However, high-quality GaN-based UV photodetectors could only be prepared on a sapphire substrate, which is much more expensive as compared with a glass substrate. On the other hand, the photocurrent-to-dark-current contrast ratio of ZnO-based UV photodetectors is still low. Titanium dioxide [TiO₂] is a potentially useful wide direct-bandgap material (3.2 eV for anatase and 3.0 eV for rutile) for UV photodetectors, solar cells, and gas sensors due to its outstanding physical, chemical, and optical properties [8-10]. TiO₂ is a nontoxic naturally n-type semiconductor material which has a high-temperature stability and low-production costs.

For two-dimensional [2D] films, TiO₂ UV photodetectors such as metal-semiconductor-metal detectors and Schottky barrier diodes have been demonstrated [11,12]. It is difficult to produce p- and n-type materials simultaneously, which is necessary for certain device

applications. Zhang et al. reported the formation of a 2D TiO₂/Cu₂O composite film for a photocatalyst application using the metal ion-implantation method [13-15]. Cuprous oxide [Cu₂O] is naturally a p-type direct-bandgap semiconductor with a cubic crystal structure and a room-temperature bandgap energy of 2.17 eV [16], which makes it ideal for TiO₂-based p-n heterojunctions. Cu₂O can be deposited using methods such as thermal oxidation, anodic oxidation, sputtering, solution growth, sol-gel, and electro-deposition [17-24]. Among these methods, sputtering is commonly used in the semiconductor industry. By carefully controlling the growth parameters, high-quality 2D Cu₂O films can be produced by direct-current [DC] sputtering [18].

Recently, one-dimensional oxide semiconducting materials have attracted a lot of attention for potential application in optoelectronic devices due to their large surface-area-to-volume ratio [25]. Wu et al. reported the growth of TiO₂ nanowires [NWs] on glass substrates by the thermal oxidation-evaporation method [26,27]. They produced single-crystalline TiO₂ NWs, whose size and density were controlled by adjusting the growth parameters. However, no report on the fabrication of p-Cu₂O-shell/n-TiO₂-nanowire-core heterojunction UV photodetectors could be found in the literature, to our knowledge. The present study reports the deposition of p-Cu₂O film onto n-TiO₂ NWs by DC sputtering and the fabrication of radial p-Cu₂O-shell/n-TiO₂-nanowire-core photodiodes. The physical, electrical, and optical

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properties of the fabricated radial p-Cu₂O-shell/n-TiO₂-nanowire-core photodiodes are discussed.

Experimental section

Before the growth of TiO₂ NWs, a Corning 1737 glass substrate (Corning Display Technologies Taiwan Co., Ltd., Taipei City, Taiwan) was wet-cleaned with acetone and deionized water. The glass substrate was subsequently baked at 100°C for 10 min to evacuate moisture. A 400-nm-thick titanium [Ti] film layer was then deposited onto the glass substrate by electron-beam evaporation. Finally, the samples were annealed in a furnace at 700°C for 3 h to synthesize TiO₂ NWs in argon [Ar] ambiance. The crystal quality of the as-grown NWs was then characterized by an X-ray diffractometer [XRD] (MXP 18, MAC Science Co., Tokyo, Japan). The surface morphology of the samples and the size distribution of the NWs were characterized by a field-emission scanning electron microscope [FE-SEM] (JEOL JSM-7000F, JEOL Ltd., Tokyo, Japan).

To investigate the deposition of Cu₂O, glass was used as the substrate. The target used to deposit Cu₂O was a 4-N pure copper block mounted on the cathode. The distance between the target and the sample was fixed at 60 mm. A rotating magnet fixed on the backside of the cathode was used to enhance the plasma bombardment effect. During sputtering, the Ar flow rate, deposition time, base pressure, and chamber pressure were kept at 15 sccm, 10 min, 2×10^{-6} Torr, and 6 mTorr, respectively, and the DC power, O₂ flow rate, and substrate temperature were 200 W, 4 sccm, and 25°C, respectively. The crystallography and structure of the deposited Cu₂O and the Cu₂O/TiO₂ NWs were evaluated by XRD and FE-SEM.

Prior to the fabrication of p-Cu₂O-shell/n-TiO₂-nanowire-core photodiodes, a small piece of glass was used to cover the TiO₂ NWs to prevent the deposition of Cu₂O in these regions. A 200-nm-thick Cu₂O layer was subsequently deposited onto the TiO₂ NWs. A 500-nm-thick silver layer was then sputtered onto the Cu₂O layer and TiO₂ NWs to serve as the p-electrode

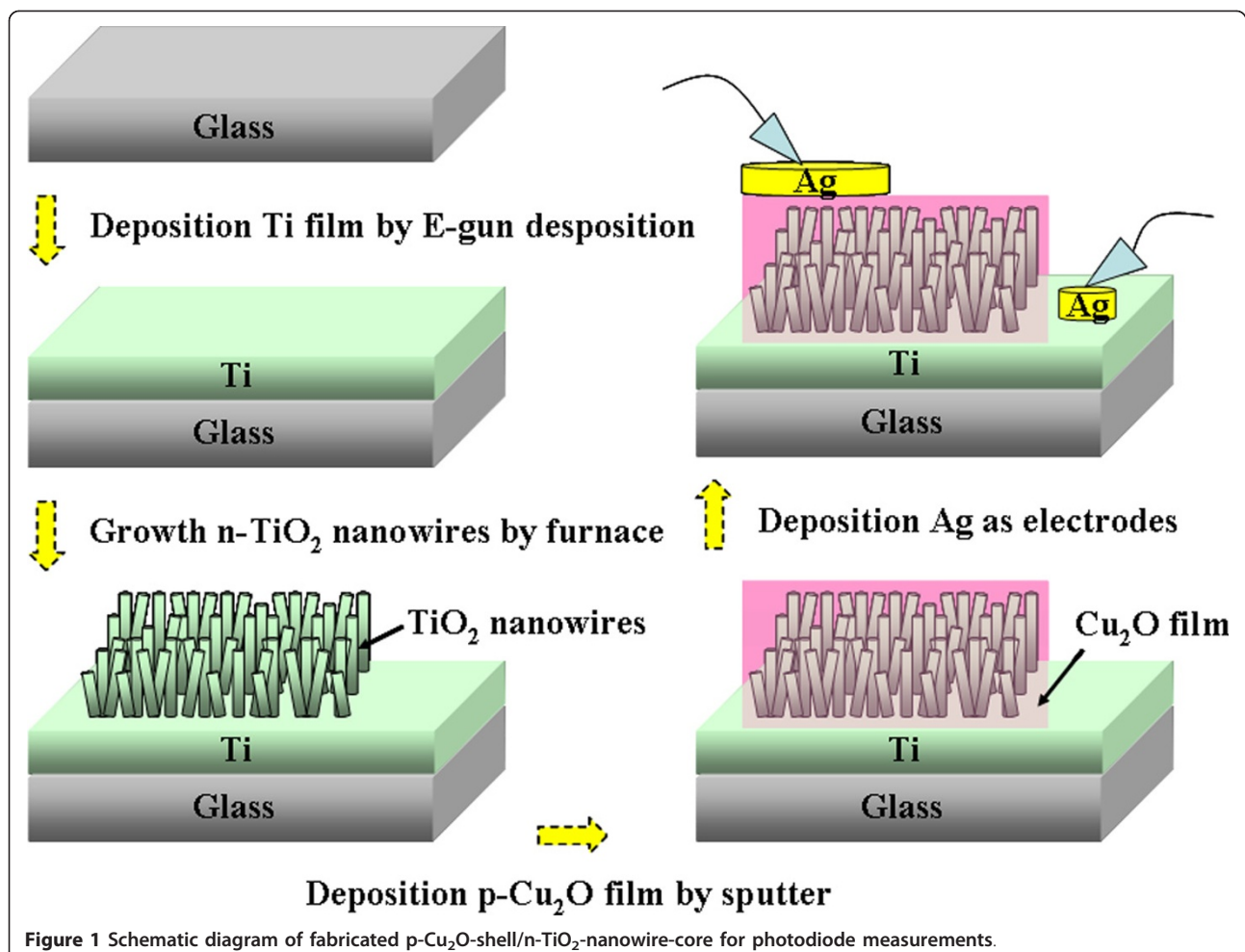
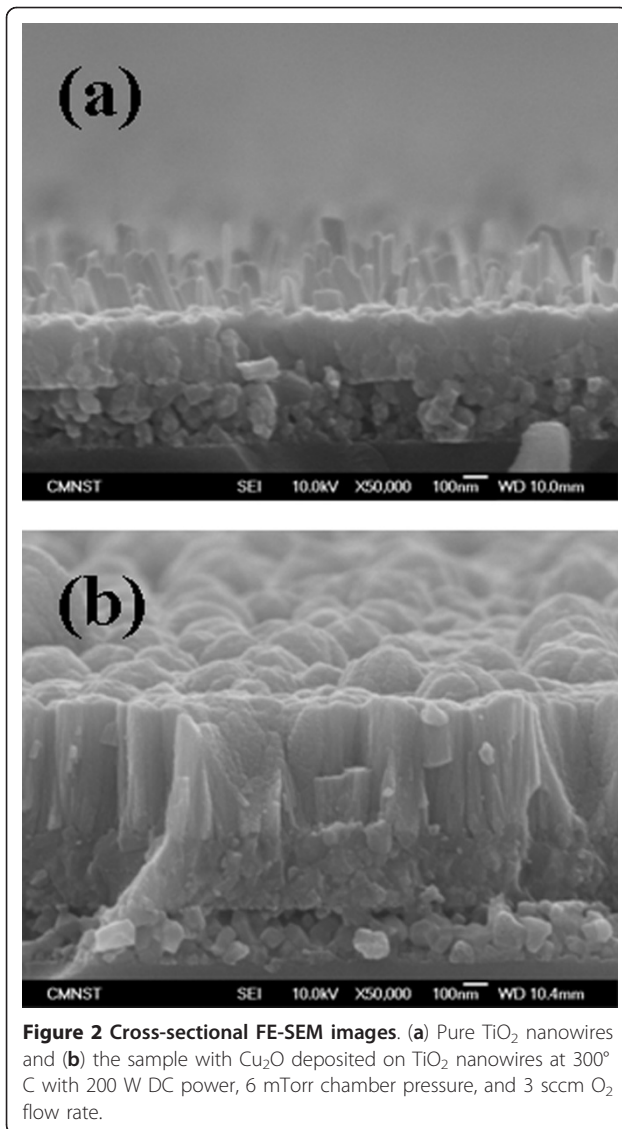


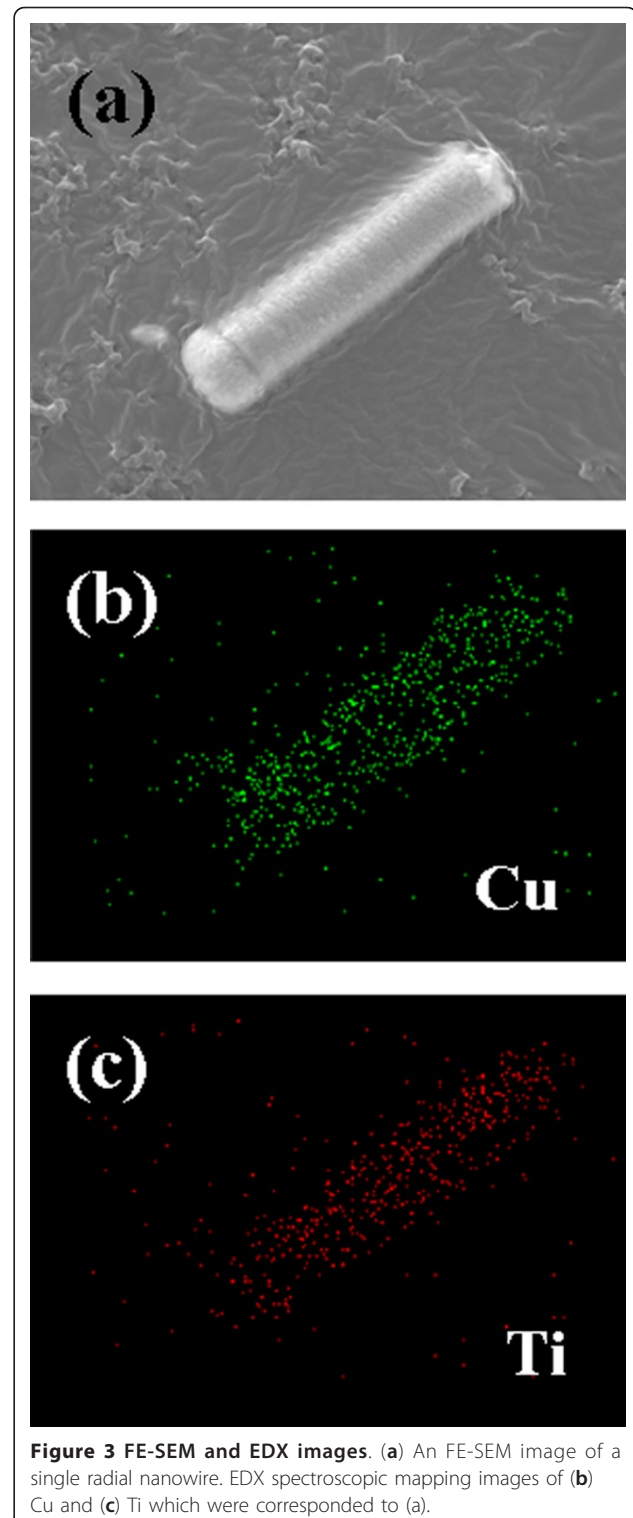
Figure 1 Schematic diagram of fabricated p-Cu₂O-shell/n-TiO₂-nanowire-core for photodiode measurements.



and n-electrode with a shadow mask. Figure 1 schematically shows the structure of the fabricated p- Cu_2O -shell/n- TiO_2 -nanowire-core photodiodes. A picoammeter (HP-4145B semiconductor parameter analyzer, Agilent Technologies, Sta. Clara, CA, USA), connected via a GPIB controller to a computer, was then used to measure the current-voltage [I-V] characteristics of the fabricated diodes under darkness. The photo responses of the devices were also measured. During photo-response measurements, a 4-W mercury vapor lamp emitting at 365 nm was used as the excitation source.

Results and discussion

Figure 2a shows a cross-sectional FE-SEM image of the TiO_2 NWs prepared on a Ti/glass template. It can be clearly seen that high-density TiO_2 NWs of various



lengths were grown on the Ti/glass template. As shown in Figure 2a, it can be seen that the average length, diameter, and density of these TiO_2 NWs were $0.3\ \mu\text{m}$, 50 nm, and $60\ \text{wires}/\mu\text{m}^2$, respectively. Figure 2b shows a

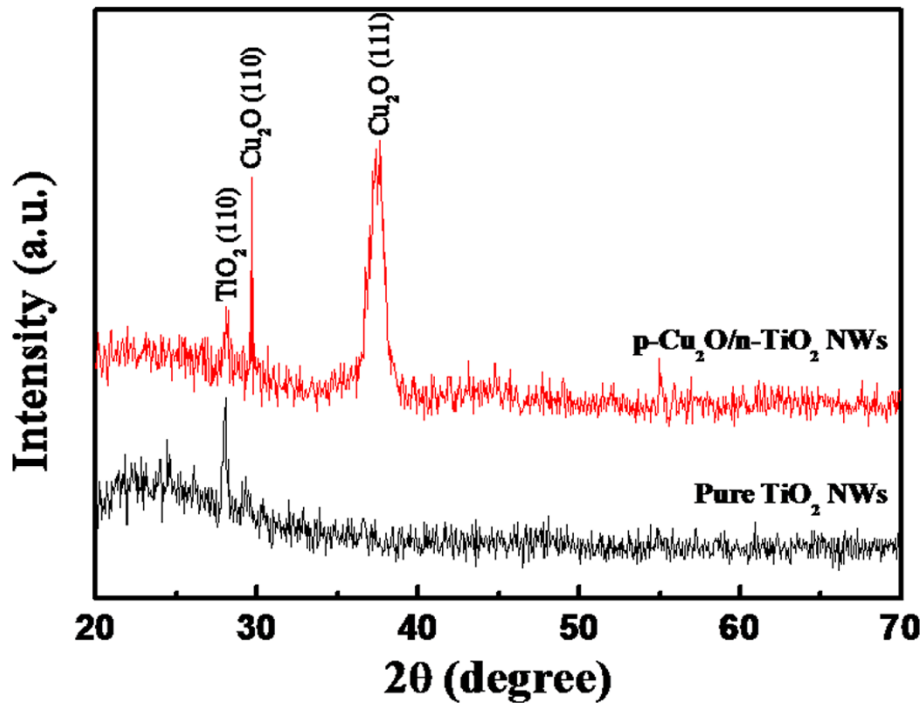


Figure 4 XRD measurements of pure TiO₂ nanowires and p-Cu₂O/n-TiO₂ nanowires obtained by DC sputtering.

cross-sectional FE-SEM image of the sample with Cu₂O deposited on TiO₂ NWs. As shown, the deposited Cu₂O filled the gaps between the TiO₂ NWs with good step coverage to form radial Cu₂O/TiO₂ NWs. It was also

found that the deposited Cu₂O formed at the sample surface after filling the gaps. In order to investigate the coating performance of Cu₂O, the deposited sample was scraped with tweezers into an alcohol solution, which

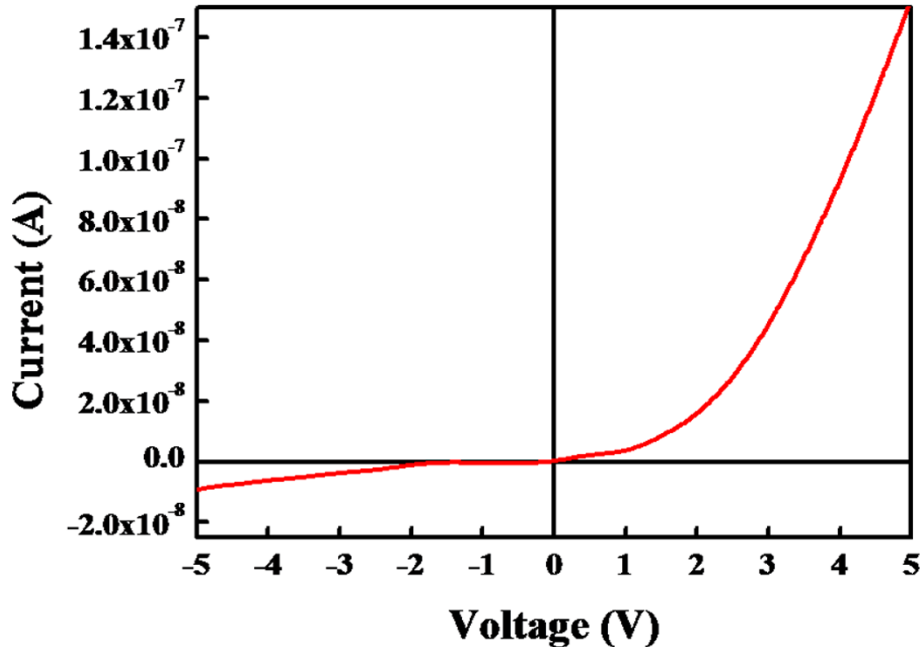


Figure 5 Dark I-V characteristic measured from the fabricated radial p-Cu₂O/n-TiO₂ nanowires.

was then ultrasonically treated for 20 min to disperse the NWs. The solution was dropped on carbon tape which was then placed on a hot plate to evacuate the alcohol. Figure 3a shows a SEM image of a single NW. Figures 3b and 3c show energy-dispersive X-ray [EDX] spectroscopic mapping images of Cu and Ti, respectively. These figures correspond to the SEM image shown in Figure 3a. After the deposition of Cu_2O , Cu and Ti atoms were distributed over the entire NW. These results suggest that the sputtered Cu_2O not only forms the head portion of the nanoclubs, but also forms nanoshells surrounding the TiO_2 cores in the nanowire portion of the nanoclubs. The formation of such p- Cu_2O -shell/n- TiO_2 -nanowire-core heterostructure should be able to provide us with a large junction area, which is important for the application of photodetectors.

Figure 4 shows the crystallographic characteristics obtained from XRD measurements. For the pure TiO_2 NWs used for adhesion, the peaks were attributed to the rutile- TiO_2 (110) phase (JCPDS Card No. 88-1175). For the p- Cu_2O /n- TiO_2 NWs, the peaks were attributed to the (110) and (111) phases of the Cu_2O phase (JCPDS Card No. 78-2076). No Ti-related signal was found, indicating that the Ti film changed into a TiO_2 film after the annealing process.

Figure 5 shows the dark I-V characteristics measured from the fabricated radial $\text{Cu}_2\text{O}/\text{TiO}_2$ NWs. The rectifying behavior indicates that a p-n junction formed in the $\text{Cu}_2\text{O}/\text{TiO}_2$ NWs. The operation of the photodiode

detector involves three steps (1) the generation of electron-hole [$e-h$] pairs by the absorption of incident light, whose photon energy exceeds the bandgap of the materials in the device; (2) the separation and transport of the $e-h$ pairs by the internal electric field; and (3) the interaction of current with the external circuit to generate an output signal. Hence, the I-V characteristics of a photodiode in a dark environment are similar to those of a normal rectifying diode. If the p-n junction does not form, the generated $e-h$ pairs will exhibit an ohmic character in the I-V curve and change the resistance. When a photodiode with a p-n junction is illuminated with optical radiation, the I-V characteristics shift according to the photocurrent and reverse current. The measured current in the photodiode, I_m , is:

$$I_m = I_d - I_{ph}$$

where I_d is the dark current and I_{ph} is the photocurrent. The presence of a reverse current indicates that the photo response is due to the p-n junction, not the TiO_2 NWs or the Cu_2O . In the process of measurement under illumination, UV light passes through the TiO_2 and illuminates the array of the radial p- Cu_2O /n- TiO_2 NWs; $e-h$ pairs are produced in the radial NWs when the energy of the UV light is absorbed. The $e-h$ pairs are separated by the internal electric field, and a photocurrent is simultaneously generated. Under forward bias, the turn-on occurred at approximately 0.9 V. With a +5-V applied bias, the forward current of the device was

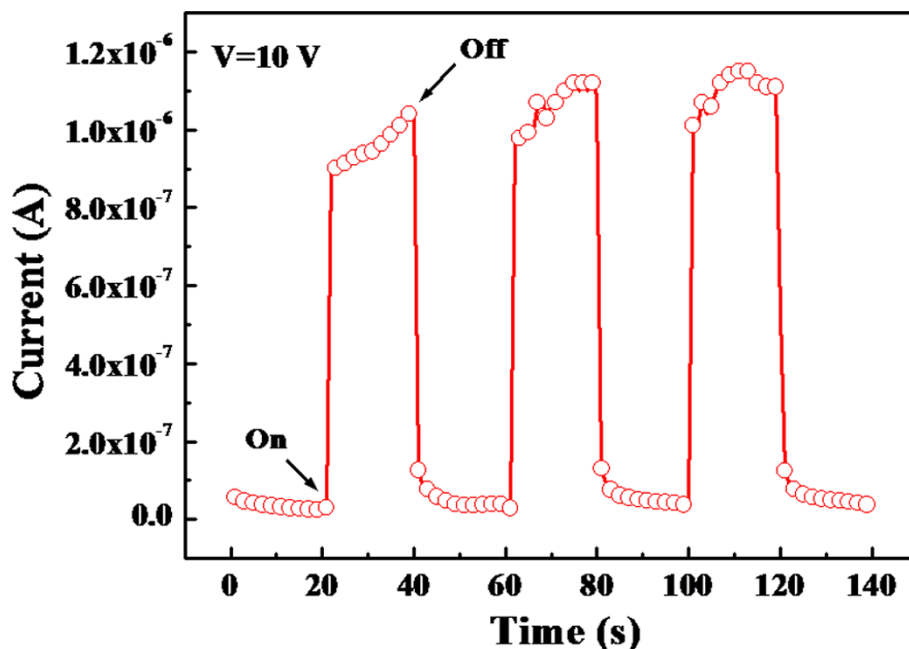


Figure 6 Dynamic photo response measured from the fabricated p- Cu_2O -shell/n- TiO_2 -nanowire-core photodiode.

1.53×10^{-7} A, and with a -5-V applied bias, the reverse leakage current was 7.74×10^{-9} A.

Figure 6 shows the dynamic photo response measured from the fabricated p-Cu₂O-shell/n-TiO₂-nanowire-core photodiode. With a +10-V applied bias, the dark reverse leakage current of the diode was only around 3.37×10^{-8} A. However, the reverse leakage current increased rapidly to 1.15×10^{-6} A upon UV illumination. When the UV lamp was turned off, the reverse leakage current rapidly decreased to its original value. The reasonably large photocurrent-to-dark-current contrast ratio and the fast responses suggest that the radial p-Cu₂O-shell/n-TiO₂-nanowire-core photodiodes proposed in this study are potentially useful for UV detector applications.

Conclusions

The deposition of Cu₂O onto well-aligned TiO₂ NWs by DC sputtering was reported. With the proper sputtering parameters, the deposited Cu₂O filled the gaps between the TiO₂ NWs with good step coverage to form radial p-Cu₂O/n-TiO₂ NWs that exhibited rectifying I-V characteristics. The fabricated radial p-Cu₂O-shell/n-TiO₂-nanowire-core photodiodes had a reasonably large photocurrent-to-dark-current contrast ratio and fast responses.

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Authors' contributions

TYT carried out the nanowire experiments and data analysis and wrote the manuscript. SJC and TJH participated in data analysis and revised and finalized the manuscript. HTH designed the thin film and other experiments and data analysis. WYW participated in the revision of the manuscript. CLH provided the concept of the growth process of the nanowire. All the authors contributed to the preparation and revision of the manuscript and approved its final version.

Competing interests

The authors declare that they have no competing interests.

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