A potential photodetector device based on zinc oxide nanorods hydrothermally grown on a *p*-type silicon substrate

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INTRODUCTION

Continuous development of optoelectronic devices has translated to significant success in various fields of science and technology such as gravitational wave detection, advanced medical terahertz (THz) imaging, modern solar cell technologies, and high-power laser systems. As the widely used optoelectronic devices, photodetectors are regarded as one of the most integral because of their ability to precisely convert electromagnetic radiation to usable electronic signals. To contend with the decreasing scale of modern devices, recent investigations have mainly focused on utilizing nanomaterials for device fabrication [1]. Since the device performance depends largely on the inherent characteristics of the material components, material selection and device design are important towards the development of low-cost and efficient photodetectors. On the other hand, zinc oxide (ZnO) is a readily available II-VI semiconductor compound which is similar to gallium nitride (GaN) in terms of properties and applications. Its wide and direct band gap (3.37 eV) and large exciton binding energy (60 meV) enable intense and efficient ultraviolet (UV) emissions at room or higher temperatures [2]. Different fabrication procedures have then been implemented to produce a wide variety of ZnO films and nanostructures. Among these techniques, the hydrothermal growth method is a simple and versatile way to synthesize ZnO nanostructures. Unlike physical vapor deposition methods such as magnetron sputtering, pulsed-laser deposition (PLD), and metal-organic chemical vapor deposition (MOCVD), hydrothermal growth involves fabrication at low temperatures using tabletop equipment without any vacuum requirements and precise gas concentrations.

In this regard, we report the fabrication and characterization of a potential photodetector device based on ZnO nanorods hydrothermally grown on a *p*-type silicon (Si) substrate. Vertically aligned ZnO nanorods are synthesized directly on a seeded *p*-type Si substrate using hydrothermal growth method. The direct growth of highly-oriented nanostructures on a *p*-type semiconductor wafer is beneficial for mass production and integration. A heterojunction device with vertical geometry also allows the possible injection of higher currents [3] into the device and the improvement of the emission efficiency [4] with the increase in the material density or surface-to-volume ratio. Moreover, a very thin aluminum (Al)-doped ZnO film is also deposited on top of the nanorods to allow contact among the nanorod tips by creating a continuous layer above the nanostructures. Compared with previous investigations, this work specifically aims to identify the structural, optical, and electrical properties of the fabricated *p*-*n* heterojunction, to assess its performance as a potential UV photodetector, and to provide important insights on *p*-Si/*n*-ZnO heterojunction device fabrication.

FABRICATION

A *p*-Si/*n*-ZnO heterojunction was fabricated based on ZnO nanorods hydrothermally grown on a seeded (100) Si substrate. The *p*-type Si substrate was initially cleaned using trichloroethylene (C_2HCl_3), acetone (C_3H_6O), and methanol (CH_3OH) solvents through successive ultrasonication. A thin ZnO seed layer was subsequently deposited on the substrate surface via spray pyrolysis technique. The substrate was sprayed with 50 mL 50 mM zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$, ZnAc] solution every 15 s while being maintained at 350 °C for 60 min. ZnO nanorods were then synthesized on the seeded Si substrate through hydrothermal growth method. The substrate was submerged into a 200 mL mixture of 25 mM ZnAc and 40 mM hexamethylenetetramine [$(CH_2)_6N_4$, HMTA] aqueous solutions. After heating at 85 °C for 180 min, the

substrate was removed from the ZnAc-HMTA mixture, was rinsed with deionized water, and was dried in air. A 2.0 mole percentage (mol %) Al-doped ZnO thin film was soon deposited on top of the ZnO nanorods also via spray pyrolysis technique. The nanorods were sprayed with a 100 mL mixture of 50 mM ZnAc and 1 mM aluminum chloride (AlCl) aqueous solutions and were annealed at 500 °C for 30 min. Silver (Ag) contacts were deposited on the backside of the Si substrate, while indium (In) contacts were patterned as a grid with 0.3 mm finger width and 1.0 mm finger spacing on top of the Al-doped thin film.

CHARACTERIZATION

Figure 1 shows the plan-view and cross-sectional SEM images of the fabricated *p*-Si/*n*-ZnO heterojunction. The sample surface is occupied by hexagonal rod-like structures which have average widths of 480 nm and share common sides and boundaries. These nanostructures appear to be the hydrothermal-grown nanorods since there are no clear distinctions between the nanorods and the Al-doped thin film due to their relative thicknesses (i.e., the nanorod layer is much thicker than the thin film layer). Standing perpendicular to the substrate surface, the nanorods have average lengths of 1.15 μm which is also the apparent thickness of the ZnO nanorod-thin film layer. These observations suggest that the heterojunction's ZnO layer is predominantly made up of vertically aligned, hexagonal ZnO nanorods.

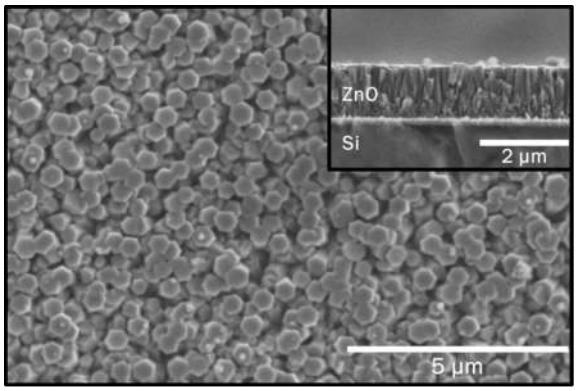

Fig. 1. SEM images of the fabricated p-Si/n-ZnO heterojunction. The heterojunction's ZnO layer is predominantly made up of vertically aligned, hexagonal ZnO nanorods.

Figure 2 depicts the TIPL spectrum of the fabricated *p*-Si/*n*-ZnO heterojunction. The heterojunction exhibits only an intense UV emission which has a peak position at 386 nm (3.21 eV) and a spectral linewidth of 30 nm. This UV emission which corresponds to the near-band-edge ZnO emission [2] is slightly red-shifted compared with the usual room-temperature ZnO emission at ~ 380 nm (3.26 eV). Strong or broad visible emissions, which are typically manifested by various defects in ZnO nanostructures and thin films, are also not observed. These results suggest that the heterojunction is fabricated with ZnO nanorods exhibiting good optical quality.

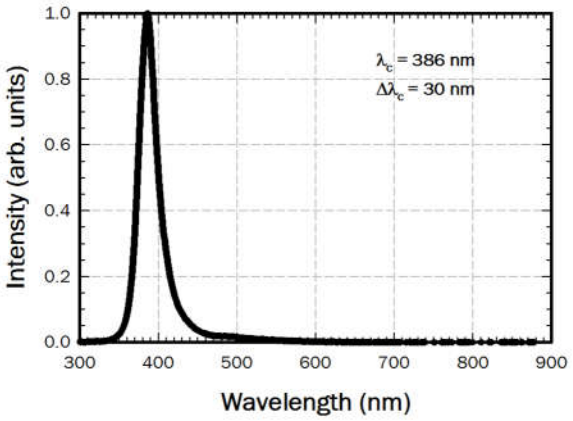

Fig. 2. TIPL spectrum of the fabricated p-Si/n-ZnO heterojunction. The heterojunction only exhibits an intense UV emission with a peak position (λ_c) at 386 nm and a spectral linewidth ($\Delta\lambda_c$) of 30 nm.

Figure 3 shows the UV emission intensity distribution of the fabricated *p*-Si/*n*-ZnO heterojunction. The heterojunction exhibits intense and fast characteristic UV emission at room temperature. From this intensity distribution, the UV emission profile which is integrated from a 30 nm spectral region around the peak position is shown in Fig. 4. A single exponential function is fitted on the decaying part of the profile to determine the UV emission lifetime. The observed lifetime is faster than those reported for undoped bulk ZnO crystals (1 to 3.5 ns) [5] and comparable to intentionally doped bulk ZnO (3.1 to less than 100 ps) [6, 7] under UV excitation. These observations suggest that the heterojunction is fabricated with ZnO nanorods exhibiting a relatively fast decay (response) time.

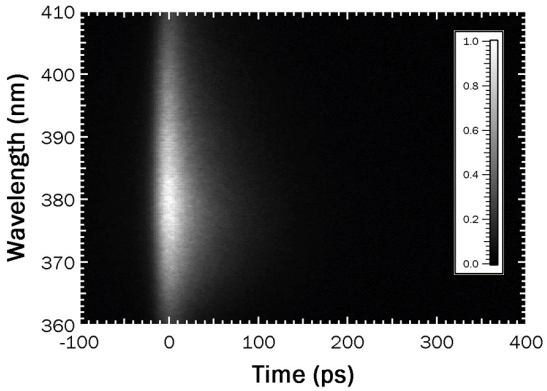

Fig. 3. UV emission intensity distribution of the fabricated p-Si/n-ZnO heterojunction. The heterojunction exhibits an intense and fast characteristic UV emission at room temperature.

Figure 5 compares the current-voltage (*I-V*) curves in the reverse bias region of the fabricated *p*-Si/*n*-ZnO heterojunction with and without UV illumination. In this operation quadrant of photodetectors, the heterojunction has higher currents with UV illumination resulting in an average contrast (photo-to-dark current) ratio of 1.21.

From 0 to -1.0 V, the measured currents are also linearly dependent on the applied voltage wherein the slope is equal to the inverse of resistance ($1/R$). Aside from higher currents, the heterojunction exhibits a lower 13 kΩ resistance (i.e., higher conductivity) with UV illumination compared to the 19 kΩ resistance without UV illumination. These results indicate that the heterojunction responds to incident UV light and that similar *p-n* heterojunction designs can be used as potential UV photodetectors.

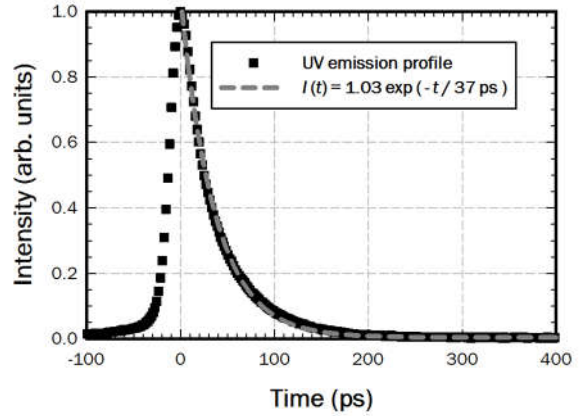

Fig. 4. UV emission profile of the fabricated p-Si/n-ZnO heterojunction. By fitting a single exponential function on the decaying part of the profile (broken gray lines), the heterojunction has been found to exhibit a UV emission lifetime of 37 ps.

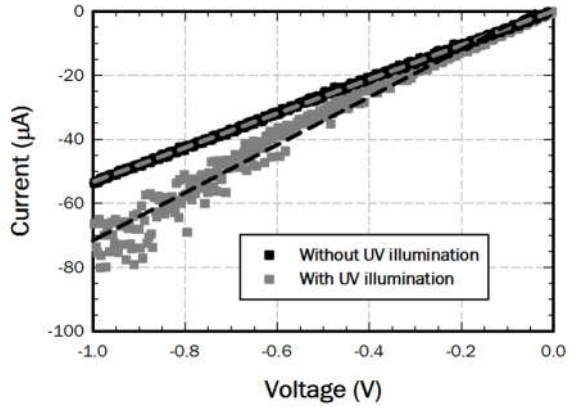

Fig. 5. I-V curves in the reverse bias region of the fabricated p-Si/n-ZnO heterojunction with and without UV illumination. In this operation quadrant of photodetectors, the heterojunction has higher currents with UV illumination resulting in an average contrast (photo-to-dark current) ratio of 1.21.

SUMMARY

We have reported the fabrication and characterization of a potential photodetector device based on ZnO nanorods hydrothermally grown on a *p*-type Si substrate. The fabricated heterojunction is predominantly made up of 1.15 μm long and 480 nm wide vertically aligned, hexagonal ZnO nanorods above the Si substrate. In addition, the nanostructures also exhibit hexagonal wurtzite crystal structure and intense 37 ps, 386 nm emission without any defect-related visible emissions. With good rectifying current-voltage behavior, the hydrothermal-grown ZnO nanorods form a *p-n* junction with the Si substrate. Furthermore, the fabricated *p*-Si/*n*-ZnO heterojunction responds to the incident UV light resulting in an average contrast ratio of 1.21 along with currents higher and resistance lower than without illumination. Similar heterojunction designs are therefore suggested to be used as potential fast-response UV photodetectors since the present approach can easily produce a high density of ZnO nanorods on larger Si wafers and is compatible with the current Si-based technologies. Additional investigations on the utilization of hydrothermal-grown ZnO nanorods as viable photodetector materials are nevertheless anticipated in the future.

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