Interface architecture determined the performance of ZnO nanorods-based photodetectors

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Abstract

High density ZnO nanorods grown on silicon oxide-coated Si (111) substrates were used to fabricate an MSM UV photodetector. The maximum sensitivity of the detector was about 1150, which was maintained over the wide range of applied bias. The photodetector responsivity increased slightly until reaching a maximum value at 374 nm and exhibited a sharp cutoff at 378 nm. The obtained photodetector responsivity was as high as 1.1 A/W. The detector shows fast photoresponse with a rise time of 0.008 s and a decay time of 0.021 s.

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1. Introduction

The mutual advantages of wide direct band gap (3.37 eV), high exciton binding energy (60 meV), and strong room temperature emission characteristics of ZnO led to numerous in-depth studies to synthesize a variety of ZnO nanostructures [1–7]. Among these various morphologies, the one-dimensional (1D) ZnO nanorods have recently attracted significant attention due to their unique shape and structure resulting in remarkable optoelectronic, piezoelectric, and magnetic properties [8–14]. Specifically, the high optical gain of ZnO makes it the material of focus in sensing and optoelectronics applications. A number of researchers have focused mainly on the ZnO-based metal–semiconductor–metal (MSM), which includes ohmic contact-based photoconductive type. Xu et al. [15] reported RF sputtered ZnO on quartz to fabricate a photoconductive UV detector with planar interdigitated Al electrodes. The current–voltage (I–V) measurements showed a dark current of only 38 μA, which increased to 882 μA upon illumination (365 nm) at an applied bias of 5 V. Sputtering Au as a catalyst onto the quartz substrate, Li et al. [16], was able to fabricate a nanowatt UV photodetector. He et al. [8] reported a photocurrent of 0.15 mA using a more complex structure (glass/Ag/ZnO seed layer/ZnO nanowires). Based on the reported devices, it seems that the interface architecture is the limiting factor. This limitation can be related to the crystal mismatch between ZnO and most of the tested substrates. Therefore, the current study proposed a method to overcome such limitations by using a thin film ZnO buffer layer, to avoid crystal mismatch and enhance the integration of ZnO nanorods in UV photodetectors. More advantages of growing ZnO nanorods on SiO2-coated Si (111) substrates include the low cost preparation approach for high-gain UV photodetectors and the ease of device integration, which is compatible with the existing silicon technology.

2. Experimental procedure

After the standard RCA cleaning of the n-type Si (111) substrate, a 200-nm SiO2 layer was deposited on its surface by RF sputtering. High-purity zinc powder (1 g, 99.999%, Sigma–Aldrich) was then thermally evaporated on the Si/SiO2 substrate using vacuum thermal evaporator. The resulting sample (Si/SiO2/Zn) was successively transferred into a thermal tube furnace for oxidation at 700 °C and O2 flow rate of 5 l/min for 90 min, and then cooled to room temperature. The resulting Si/SiO2/ZnO film was used as the substrate to grow ZnO nanorods. The substrate was placed in a small quartz tube (25 cm in length and 2 cm in diameter), which was inserted inside the furnace, as described in detail in our previous studies [17,18]. The furnace temperature was gradually increased from room temperature to 900 °C at a rate of 10 °C/min under the flow of N2 gas (1 l/min), and then maintained at 900 °C under the flow of O2 gas (0.2 l/min) for 90 min. Finally, the furnace temperature was cooled to room temperature under natural conditions.

The morphological and crystallinity of the ZnO nanorods were characterized using scanning electron microscopy (SEM) JEOL.
model JSM-6460LV and X-ray diffraction (XRD) (PANalytical X’Pert PRO diffractometer, with Cu Kα radiation), respectively. The photoluminescence (PL) spectra were recorded with a He–Cd laser (325 nm) at room temperature. The MSM photodiode consists of two interdigitated electrodes with four fingers each. Each finger is 230 μm wide and 3.3 mm long, and the spacing between each finger is 400 μm. Silver (Ag) contacts were deposited by vacuum thermal evaporation using a metal mask based on the pattern of the contact structure. The device was then annealed at 425 °C for 5 min under N₂ atmosphere. The spectral UV photoresponse of the fabricated ZnO photodetector was measured using a monochromator with a 150 W xenon lamp as UV light source. A Keithley – 2400 source meter unit was employed to measure the photocurrent. The unit was controlled by a PC using LABVIEW via a GPIB interface. The measurements were performed at ambient conditions (temperature was 25 °C, and humidity was 62%).

3. Results and discussion

3.1. Characterization of the ZnO nanorods

Figure 1a,b shows the typical SEM images of the ZnO buffer layer and nanorods, respectively that were grown on Si (111)/SiO₂ substrates. High density ZnO nanorods with average diameters of 200 nm were successfully obtained. No delamination was observed, which highlights the importance of the ZnO buffer layer in preventing the direct growth of ZnO nanorods on non-crystalline SiO₂ substrates due to the importance of ZnO nanorods on SiO₂ substrates in optoelectronic applications.

The crystal quality and orientation of the grown ZnO buffer layer and nanorods on Si (111)/SiO₂ substrates were analyzed by XRD. Figure 2a,b shows the obtained XRD patterns of grown ZnO buffer layer and nanorods on Si (111)/SiO₂ substrates, respectively. The obtained diffraction peaks can be related to crystalline ZnO with hexagonal wurtzite structure, which agrees with the Joint Committee on Powder Diffraction Standards card for ZnO (JCPDS card no.-36–1451) [19,20]. The relatively high diffraction intensity obtained for both samples were in the (100), (002), and (101) planes. The ZnO nanorods diffraction pattern showed sharp and more intense peaks compared to those of the ZnO buffer layer. The narrow full width at half maximum of those peaks indicates the good crystallinity of the grown nanorods. This result also reveals the importance of the interface architecture in eliminating the effect of amorphous SiO₂ layer.

Figure 3a,b shows the room temperature PL spectra of the ZnO buffer layer and nanorods grown on the Si (111)/SiO₂ substrates, respectively. The PL emission spectrum revealed strong UV emissions at 372 nm and 374 for ZnO buffer layer and nanorods, respectively, which correspond to the near-band-edge (NBE) emission of ZnO. This obtained UV strong emission, coupled with a weak broad green (DLE) emission bands at ~520 nm (sub-band transition) for ZnO buffer layer and nanorods may indicate the high crystal quality [18,19]. As the growth was performed using Zn powder under N₂ gas flow until the furnace reached 900 °C, the oxygen vacancies (the defects favorable to form under Zn-rich conditions) are expected to be the main reason for the emergence of the green emission (DLE). However, the energy intervals between these defect levels and valence band edge are ~0.9 eV [20,21], suggesting
that the observed emission peaks at 520 nm should be assigned to the electron transition from the bottom of the conduction band to the O vacancy level. This finding is also confirmed by the high NBE-to-DLE ratio. Comparing the results obtained for the samples with and without the ZnO buffer layer indicates the part played by the interface architectures in the improvement of the structural and optical properties.

3.2. Characteristics of the ZnO nanorod MSM UV photodetector

Figure 4 shows the schematic of the ZnO nanorod MSM UV photodetector, as well as the Ag finger contacts deposited on top of the ZnO nanorods. Figure 5a shows the I–V characteristics of the fabricated PD under dark and UV illumination (365 nm, 1.5 mW) conditions at room temperature. The obtained photocurrent (0.6 mA at 5 V) was higher than the dark current (0.52 μA at 5 V) over the entire range of applied bias. This result is in agreement with Schottky-type detectors, which usually show very low dark currents because of the high material resistivity and Schottky barrier height (SBH). The low dark current helps to enhance the signal-to-noise ratio (S/N) of the detector as the shot noise is proportional to the dark current. Note that the obtained photocurrent (0.6 mA at 5 V) is four times higher than that reported by He et al. (0.15 mA at 5 V) for their glass/Ag/ZnO seed layer/ZnO nanowires photodetector [8], highlighting again the importance of the interface architecture in determining the efficiency of the PD.

The obtained I–V curves can be understood based on the thermionic emission theory, where [22–24]:

\[
I = I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right]^{-1}
\]

where \(I_0\) is the saturation current, \(q\) is the electron charge, \(V\) is the voltage across the diode, \(n\) is the ideality factor, \(k\) is Boltzmann’s constant, and \(T\) is the temperature in Kelvin. \(I_0\) is given by:

\[
I_0 = AA^*T^2 \exp \left[ -\frac{q\phi_B}{kT} \right]
\]

where \(A\) is the contact area (1.5 \text{ x } 10^{-4} \text{ cm}^2), \(A^*\) is the effective Richardson constant, and \(\phi_B\) is the SBH. In plotting \(\ln(I)\) versus \(V\) of the same set of data depicted in Figure 5a, a straight line with a slope of \(q\phi_B/kT\) and an intercept (where \(V = 0\)) of \(\ln(I_0)\) can be obtained. Given that \(I_0\) is known, SBH can be calculated using Eq. (2). The theoretical value of \(A^*\) for ZnO is 32 A/(cm² K²). Table 1 summarizes the dark current and photocurrent measured at 5 V, as well as the ideality factor and SBH of the ZnO nanorod samples. The high photocurrent obtained can be related to the observed decrease in \(\phi_B\) and \(n\) values under illumination. This finding is also confirmed by calculating the contrast ratio (sensitivity), photo-to-dark current, of the photodetector.

Contrast ratio (CR) is an important parameter that determines the quality of the photodetector [24–26]. In this regard, the device showed a very high CR of 1150 for the forward applied voltage under UV (365 nm, 1.5 mW) illumination at room temperature over a wide range of applied bias. This value reflects the good quality of the fabricated photodetector. Measurements for ZnO nanorods showed a high material resistivity in the dark, with a series resistance of 9.7 MΩ. However, this resistance was significantly reduced to 8 kΩ upon illumination.

Responsivity (\(R\)), the ratio of the device photocurrent (\(I_p\)) to the incident optical power (\(P_{opt}\)), is another performance metric used to characterize photodetectors [27]:

\[
R = \frac{I_p}{P_{opt}}
\]

Figure 5b shows the variation of \(R\) as a function of wavelength for the ZnO NRs PD with Ag contact. The photodetector \(R\) increased slightly until it reached the maximum at 374 nm, followed by a gradual decrease. At shorter wavelength, absorption coefficient increased and the penetration depth of the UV light became shallower, thereby increasing only the carrier concentration near the film surface and consequently producing carriers with shorter lifetime due to surface recombination and hence, led to the observed drop in \(R\). A sharp cut-off at 378 nm was observed that matches the absorption edge of ZnO and agrees with the PL results shown in Figure 3. The \(R\) dropped considerably above the cut-off wavelength, indicating that a photoconductive UV detector with high sensitivity was achieved. The obtained \(R\) in this study was 1.1 A/W, more than 20 times higher.

Table 1

<table>
<thead>
<tr>
<th>Test condition</th>
<th>Ideality factor ((n))</th>
<th>(\phi_B) (eV)</th>
<th>(I) (A)</th>
<th>(R) (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark</td>
<td>1.8</td>
<td>0.70</td>
<td>5.2 \times 10^{-7}</td>
<td>9.7</td>
</tr>
<tr>
<td>UV-light</td>
<td>1.4</td>
<td>0.57</td>
<td>6.01 \times 10^{-4}</td>
<td>0.008</td>
</tr>
</tbody>
</table>
than those reported for ZnO nanorod-based photodetectors \[4,22,24,25,28–31\]. This high \( R \) can be attributed to the effect of the ZnO buffer layer and SiO\(_2\). \( R \) can also be defined as \[32\]:

\[
R = \eta \frac{q^2}{h c G} \tag{4}
\]

where \( \eta \) is the external quantum efficiency, \( q \) is the electron charge, \( \lambda \) is the incident light wavelength, \( G \) is the photoconductive gain, \( h \) is the Planck’s constant, and \( c \) is the speed of light. According to Eq. (4), the quantum efficiency is not more than 1, implying that the high responsivity of the photodetector originated from high internal gain \[29,32,34\]. The large photocurrent density as well as responsivity can be ascribed to more carriers collected under illumination in the ZnO nanorod films. The response in the UV region was due to the band-to-band transitions in the ZnO nanorod films. Another contributing factor for the high current gain is the fact that the presence of SiO\(_2\) layer served as an insulator to confine the generated carriers within the active layers.

As the photoconductive response is another key figure of merit for a photodetector, the optical response was studied using dynamic response time measurements via exposing the device to a pulse at 365-nm UV light (1.5 mW) illumination at applied bias of 1, 3 and 5 V to test the reversibility of the photodetector. Figure 6 shows the obtained photoresponse as a function of time while the UV light was switched on and off at constant durations. The measured current rapidly increased upon exposure to UV light, and then decreased under dark conditions. Table 2 shows the values of measured rise (8 ms at 3 V) and decay (21 ms at 3 V) times of the (Ag–ZnO NRs–Ag) UV detector. Note that the obtained rise and decay times are much better than those reported for ZnO buffer layer–free photodetectors by Soci et al. \[34\] for CVD-deposited ZnO nanowires (23 s and 33 s, respectively) and Ozgür et al. \[35\] for the pulsed laser deposited-ZnO (50 s and 120 s, respectively). This may indicate the importance of the ZnO buffer layer in improving the photoresponse of ZnO-based PDs.

The simplest and most commonly accepted theory for the ZnO nanorod detector operation mechanism is that oxygen molecules (O\(_2\)) are initially adsorbed on the nanorod surface as negatively charged ions by capturing electrons from the n-type ZnO. When the incident photons are absorbed inside ZnO nanorods, electron–hole pairs are generated. The photogeneration is governed by the adsorption–desorption of oxygen at the ZnO surface, resulting in the formation of a transversal depletion layer between the nanorod axis and the negatively charged surface. The photogenerated holes are then driven by the depletion field to the surface and combine with the surface oxygen ions. The enhancement in photocurrent was determined by several factors such as the enhanced light absorption by ZnO nanorods, the enhanced electron–hole pair generation under UV illumination because of the size confinement effect, and the enhanced surface-state trapping due to the high surface-to-volume ratio of the ZnO nanostructure \[36\]. To this end, Schottky barrier demonstrates hole-trapping in the reversed bias junction, which reduces the depletion region and assists the tunneling of additional electrons \[8,22,32–34\]. The nanostructures can also have potential in optoelectronic switches, with the insulating state as ‘OFF’ in the dark and the conductive state as ‘ON’ when exposed to UV light. The current rise in the ZnO nanostructures under UV exposure can be attributed to the increase in the charge carrier density caused by the introduction of additional photogenerated electrons, together with the lowered barrier height caused by photo desorption of negatively charged surface oxygen. However, the current decay in dark condition can be attributed to chemisorptions of oxygen on the surface of ZnO nanostructures that capture electrons from the ZnO nanorods \[8\].

### 4. Conclusions

In summary, we demonstrate the fabrication of high quality UV detector based on highly dense ZnO nanorods grown on SiO\(_2\)/Si (1 1 1) substrates. The ZnO nanorods were fully examined and indicated a high crystalline quality with hexagonal wurtzite structure. The ZnO buffer layer has been held responsible for the observed high quality of the fabricated ZnO nanorods. In addition, the SiO\(_2\) insulator layer reduced the possibility of oxygen migration into ZnO nanorods. The fabricated Ag–ZnO NRs–photodetector showed a high sensitivity for UV light. The responsivity (\( R \)) was found to be 1.1 A/W at 5 V bias, which is an indicator of high internal gain. Again, SiO\(_2\) was held responsible in contributing to the obtained high gain by confining the generated carriers within the active layers. Under low power illumination (365 nm, 1.5 mW), the device showed a relatively fast response (8 ms) and baseline recovery (21 ms) times for UV detection. The prototype device shows a simple method for highly dense nanorods synthesis and demonstrates the possibility of constructing nanoscale photodetectors for nanoptics applications.

### References


![Figure 6](image-url)