AIP Applied Physics Letters

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Citation: Applied Physics Letters **105**, 083106 (2014); doi: 10.1063/1.4893944
View online: http://dx.doi.org/10.1063/1.4893944
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/105/8?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **105**, 083106 (2014)

Investigation of the electrical switching and rectification characteristics of a single standalone n-type ZnO-nanowire/p-Si junction diode

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(Received 16 June 2014; accepted 12 August 2014; published online 25 August 2014)

In this work, n-ZnO-nanowire/p-Si junction diodes have been fabricated and characterized both physically as well as electrically. The measurements are performed on a single standalone nanowire diode for the investigation of electrical transport through the nano-junction. The rectification properties of the single n-ZnO nanowire/p-Si diode have been studied for various input waveforms and frequencies. The diodes exhibit very promising rectification as well as switching behavior with no charge storage effect and consequently, a switching time as small as ~1 ms has been achieved. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4893944]

The zinc oxide (ZnO) nanostructures have attracted a great deal of interests from researchers around the globe due to its unique properties and versatile applications in the areas of transparent electronics, optoelectronics, piezoelectrics, chemical sensing, and spintronics devices.[1–5] Different types of ZnO nanostructures including nanowires, nanotubes, nanobelts, nanopropellers, and nanocages[6–10] have been studied. Among these, the nanowire structures are of particular interest due to their unique properties in terms of defined geometry, ability to create arrays, and potential to fabricate electronic devices such as diodes and transistors.[11,12] The large band gap energy (3.37 eV) and high excitonic binding energy (60 meV) of ZnO nanowires make them particularly suitable for UV laser and light-emitting diodes (LED).[13,14] Recently, Schottky diodes, fabricated using ZnO nanowires, have been demonstrated for chemical and UV light sensors.[15–19] Thus, the sustained progress of ZnO based nano-electronics research invites further investigation of both physical and electrical behavior of single nanowires for developing comprehensive understanding to bring such devices into circuit level applications.

Therefore, the development of ZnO-nanowire based elementary devices such as switches and rectifiers is very important for the fabrication of nano-electronic circuits and components. The control over fabrication and characterization of such elements on a single nanowire is crucial since such nanostructure circuit components are the integration of individual nanowire based devices. The excellent properties of ZnO nanowires can be exploited appropriately only when reliable and superior nano-devices are fabricated with such materials. In the present work, self assembled (002)-ZnO nanowires are grown by employing a cost effective approach on p-type (100)-silicon (Si) substrate. The grown nanowires are n-type in nature due to their intrinsic defects, originating from the oxygen vacancies and zinc interstitials.[20–22] Therefore, the nanowires form p-n junctions at the interface with p-Si substrate. The electrical characterization of such junction diodes is performed by measuring rectification and switching behavior of a single standalone nanowire using the standard pulse responses.

For the growth of ZnO nanowires, initially a ZnO seed layer was prepared by employing a sol-gel route where 5 mM Zinc Acetate Di-hydrate is dissolved in 50 ml of pure ethanol. The solution is stirred at 450 rpm for 5 min at room temperature, thereby, forming ZnO nanoparticles.[23] This solution is spin coated on a clean (100)-p-Si substrate at 500 rpm for 30 s and subsequently by 2000 rpm for another 30 s. After the preparation of seed layer, these samples are annealed at 250 °C in Ar environment at 10 psi pressure for 30 min to remove the solvents. Equi-molar aqueous solutions of 0.1 M Zinc Nitrate Hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and Hexamethylenetetramine ($C_6H_{12}N_4$) are prepared using 50 ml of deionised (DI) water and mixed together in a beaker, where the sample with the seed layers were dipped vertically and stirred at 250 rpm. With increasing deposition time and temperature, the transparent solution turns out to be slightly whitish due to precipitation of ZnO which finally leads to heterogeneous reaction and deposition of ZnO on Si substrate. The solution becomes whiter after a 60 min of sustained stirring at 80 °C and the deposition is performed for 120 min. The final temperature and pH level of the solution at this stage is measured to be 90 °C and 5.3, respectively. Finally, the sample is rinsed in running DI water, followed by drying up in N_2 ambient.

Surface morphology of the sample is characterized by using high resolution field emission scanning electron microscopy (FESEM) (Zeiss Auriga 39–63) technique. Fig. 1 represents the SEM micrographs of the grown ZnO nanowires on (100)-Si substrate. It is apparent from the SEM images that the grown nanowires acquire a hexagonal shape along c-axis plane. Along with the vertical ZnO hexagonal nanowires, some tipped-nanowires are also observed. The grown nanowires are highly aligned in vertical direction, confirming the c-axis oriented growth. Average thickness of

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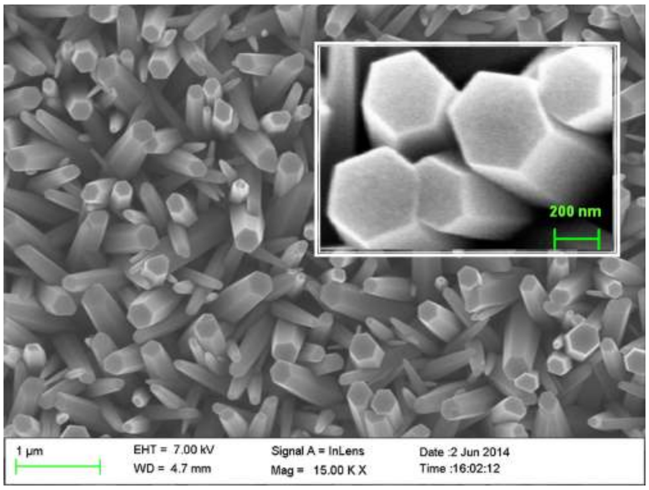

FIG. 1. The FESEM image of the grown ZnO-nanowires on p-Si substrate. Image in the inset shows the ZnO hexagonal structures.

the grown nanowires is obtained to be ≈150–250 nm and the average height is ≈1.5–1.8 μm.

X-ray diffraction (XRD) pattern of the grown ZnO nanowires are plotted in Fig. 2 which confirms the formation of wurtzite ZnO nanostructures. The peaks in the graph correspond to crystalline ZnO with [100], [002], [101], and [102] planes at $2\theta = 31.78°$, $34.42°$, $36.27°$, and $47.55°$, respectively.[24] The dominant peak from the sample is seen to appear from [002] plane, indicating highly oriented ZnO nanowire growth along c-axis.

The electrical characteristics of a single standalone n-ZnO-nanowire/p-Si diode have been measured using two tungsten (W) probe-tips attached to the Kleindiek micromanipulators (MM3A-EM) inside the FESEM chamber under high vacuum at a pressure of 10^{-6} mbars. The manipulators were attached to a Keithley-2401 Source Measure Unit (SMU). During each run of the measurement, the electron beam was blanked to avoid any background source of current. Schematics of the experimental setup is shown in Fig. 3(a) and the corresponding FESEM image is shown in Fig. 3(b). Electron affinity of ZnO and Si are 4.5 eV and 4.05 eV,

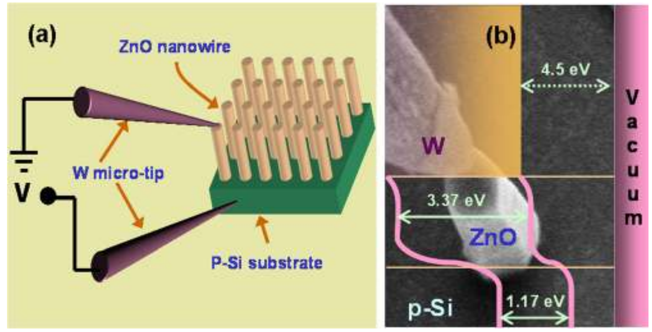

FIG. 3. (a). Schematics of the electrical measurement set up; (b) FESEM image of the tungsten (W) probe-tip in contact with a single standalone ZnO-nanowire on p-Si substrate during the measurement. The corresponding schematic band alignment across the junction is also overlapped on the structure.

respectively, whereas the work function of tungsten (W) is 4.5 eV,[3,25] leading to the formation of good ohmic contacts with the n-ZnO-nanowire/p-Si system, as illustrated in the schematic band alignment depicted in Fig. 3(b).

The variation of current in both linear- and log-scale through the (002)-n-ZnO-nanowire/(100)-p-Si junction is plotted with applied bias in Fig. 4, which clearly shows the behavior of a p-n junction diode. The cut-in voltage of the diode is measured to be 8 V which apparently seems to be very high. However, such high cut-in voltage has also been reported in the literature.[26,27] The relatively high cut-in voltage is attributed first, to the wide band gap of ZnO that leads to create a large barrier for the holes of p-Si, and second, to the presence of oxygen vacancies which are principal donors in ZnO and move away from the junction at forward bias,[28] and therefore, require higher voltage for electrons to be drifted to Si. The ON-state power extracted by the single n-ZnO-nanowire/p-Si diode is estimated to be of the order of 1 mW. The diode ideality factor is obtained to be ∼190 which anomalously higher than the conventional diodes. Such high value of ideality factor has also been found in the literature[29] which has been attributed to the recombination of carriers during multistep tunneling through the interface states at ZnO/Si heterojunction. Such recombination-tunneling current transport mechanism in a heterojunction is given by Riben-Feutch model[30,31] as follows:

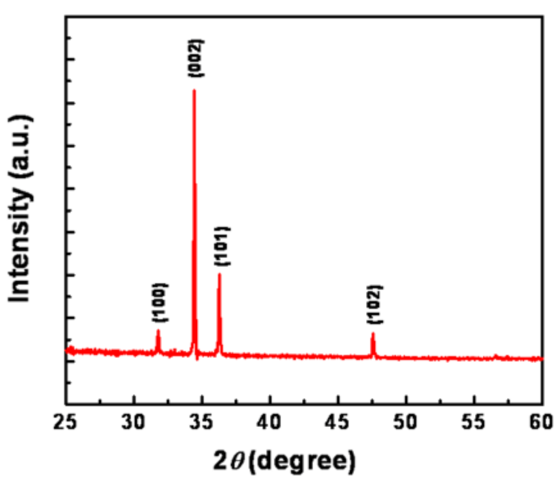

FIG. 2. Plot of the XRD pattern of ZnO nanowires. The dominant peak appearing from [002] orientation indicates the growth along c-axis or ⟨001⟩ direction.

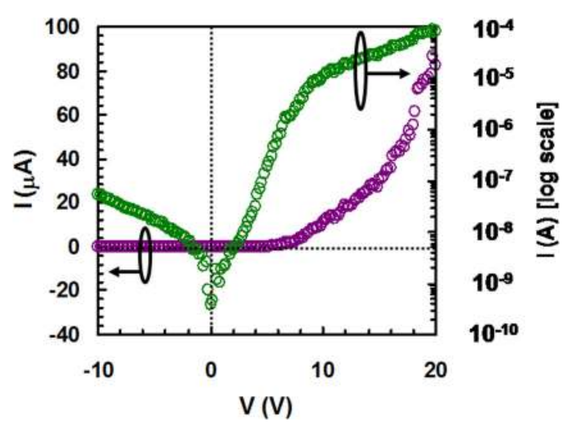

FIG. 4. Plots of the current-voltage characteristics of a single n-ZnO-nanowire/p-Si junction diode.

$$\eta = \left[\frac{kT}{q} \left[\frac{8\pi}{3h} \left\{ \frac{m^* \varepsilon_s}{N_A} \right\}^{\frac{1}{2}} \right] \frac{N_D}{N_A + N_D} \right]^{-1},$$

where q is the electronic charge, k is the Boltzmann's constant, T is the measurement temperature, h is Plank's constant, m^* is the effective mass of the carrier, and ε_s is the dielectric constant of ZnO, and N_A, N_D are the acceptor and donor concentrations. The ideality factor is estimated to be 285 using the above expression where the doping values of $N_A = 4.9 \times 10^{18}$ cm^{-3} and $N_D = 2.9 \times 10^{16}$ cm^{-3} are obtained from the experiment. For the calculation of N_A and N_D, the mobility values for Si and ZnO are taken to be $\mu_{p,Si} = 450\,\mathrm{cm}^2/\mathrm{V-s}$ and $\mu_{n,ZnO} = 200\,\mathrm{cm}^2/\mathrm{V-s}$,[32,33] respectively. Thus, the calculated ideality factor is of similar order of that ($\eta \sim 190$) obtained from I–V characteristics of the current device. Therefore, the results indicate that recombination-tunneling through interface states is the dominant factor for such deviation from the ideal behavior of the diode.

Figs. 5(a)–5(d) represent the electrical responses of the single n-ZnO-nanowire/p-Si diode to some of the standard input voltages such as sinusoidal, triangular, square, and saw-tooth wave, respectively, at the frequencies 0.025 Hz, 1 Hz, and 10 Hz. It is to be noted that the electrical response of a conventional p-n junction diode to a sinusoidal voltage is assumed to be half-sine for positive half cycle and constant equal to the reverse saturation current for the negative part. However, the diode current is an exponential function of voltage and therefore the response of n-ZnO-nanowire/p-Si diode for positive half cycle is far from half-sine due to its relatively higher cut-in voltage and diode ideality factor. It is apparent from the pulse responses plotted in Fig. 5, especially Fig. 5(c) that the device gets ON at a sharp jump with a delay of ~1 ms while the input voltage is triggered. Interestingly, no significant charge storage effect is seen and the diode behaves almost ideally as a switch. The sharp switching behavior is originated from its large barrier potential created at the junction that reduces the junction capacitance thereby lowering the delay, whereas the charge storage effect is

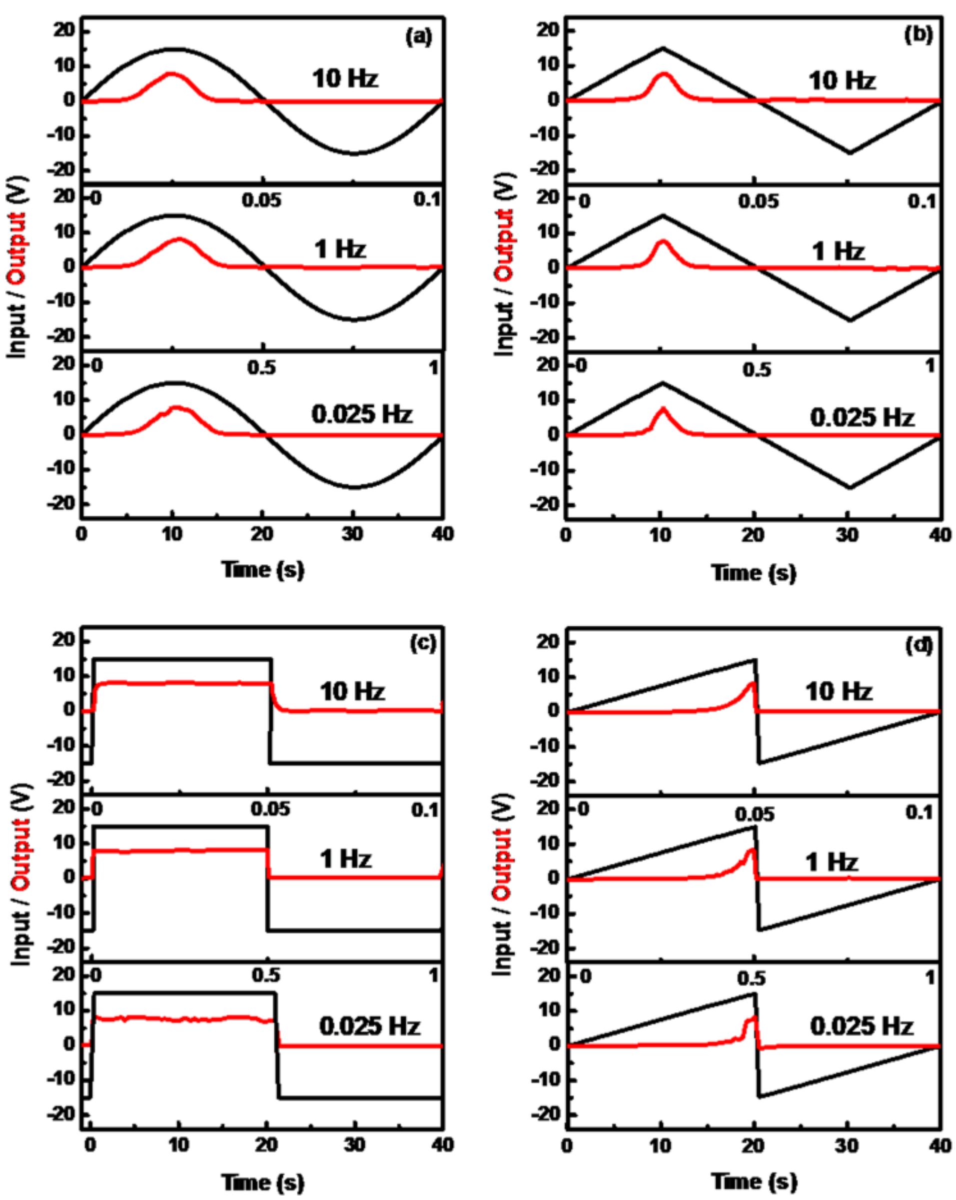

FIG. 5. Plots of output responses of the single n-ZnO-nanowire/p-Si diode in response to the standard pulses: (a) sinusoidal, (b) triangular, (c) square, and (d) saw-tooth at different frequencies.

unconventionally minimized due to extremely high recombination rate, which is consistent with the abnormally large ideality factor.

Thus, the n-type ZnO nanowires are grown on a p-Si substrate and its morphological characterization is performed using high resolution FESEM imaging and the crystal orientation is confirmed from x-ray diffraction study. The electrical measurement of a single standalone n-ZnO nanowire/p-Si diode has been performed. A high cut-in voltage of 8 V and an anomalously high ideality factor of 190 due to high band gap energy of ZnO and high interface state density have been obtained. Such diodes exhibit excellent switching properties with no charge storage effect and the switching delay as small as ∼1 ms has been found, indicating its potential to be used as a circuit element.

Mr. A. Das, Mr. B. Nag Chowdhury, Mr. M. Palit, and Ms. S. Paul like to acknowledge the University Grants Commission (UGC), India, Technical Quality Improvement Program (TEQIP), World Bank, and Department of Information Technology (DIT), India, respectively, for providing financial support to pursue their research. The authors also like to acknowledge the DST Purse program of the Department of Science and Technology, India, for providing financial support to setup the electrical characterization laboratory.

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