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Opto-Electronics Review 25 (2017) 15–18

Contents lists available at ScienceDirect

Opto-Electronics Review

journal homepage: http://www.journals.elsevier.com/opto-electronics review

Photoresistor based on ZnO nanorods grown on a p-type silicon substrate

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ARTICLE INFO

Article history:
Available online 28 February 2017

Keywords:
ZnO nanorods
Photoresistor
Hydrothermal growth
Light detection
Optical switch

ABSTRACT

In this work we discuss a method of preparation of a highly sensitive light detector based on ZnO nanorods. A photoresistor constructed by us is based on a heterojunction between high quality ZnO nanorods and high resistivity p-type Si used as a substrate for nanorods' deposition. ZnO nanorods are grown by a modified version of a microwave assisted hydrothermal method which allows for growth of high quality ZnO nanorods in a few minutes. The obtained photoresistor responds to a wide spectral range of light starting from near infrared (IR) to ultraviolet (UV). Properties of the detector are evaluated. We propose the use of the detector as an optical switch.

1. Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor with a range of possible applications. For example, it is tested for use in optoelectronics as an active material for light-emitting and detecting diodes [1]. Other applications include a new generation of electronic devices. ZnO is tested as an active part of transparent transistors [2], as a part of selector in cross-bar memories [3], as an active layer in photovoltaic devices PV [4], or as a transparent electrode [5].

Regarding applications as a light detector, the simplest construction is a photoresistor – a device changing resistance upon illumination. In consequence, photoresistors have attracted wide interest over the past three decades. A wide variety of potential applications were discussed and demonstrated. Photoresistors were used in automatic detection systems, in computer and optoelectronic control systems, for combustion process monitoring, for solar emission monitoring, for biological and chemical analysis [6–9].

The most common mechanism responsible for resistance changes is photoconduction which in the case of conventional semiconductors results in a fast detector response. This relates to a fast recombination/trapping of photo-generated electron–hole pairs. However, if resistance changes are related to surface effects, the response can be relatively slow. This is the case of some oxide materials, including n-type zinc oxide structures [10]. Resistance changes of ZnO films are primarily governed by desorption and adsorption of oxygen or hydroxyl groups. In the case of surface related effects a high surface-to-volume ratio is crucial to obtain high detector sensitivity. Not surprisingly, the sensitivity is enhanced in NRs. The latter mechanism is dominant in the case of high quality ZnO nanorods (NRs) without or with a reduced concentration of oxygen vacancies [11].

Recently, we reported a modification of a technological method allowing the growth of high-quality ZnO NRs in a controllable way. The method is very cheap, safe, and fast. Thus, it is attractive for a range of possible commercial applications [12].

Zinc oxide because of a wide band gap is commonly used in the context of the photoresistor for the UV range, but does not respond to a visible light [11,13,14]. Photoeresistors responsive to a visible light, using ZnO, are prepared on the basis of a junction with other semiconductors, for example a ZnO-Si junction [14–16]. In all these cases, the measured response is a current flow through the diode, and ZnO is often added in order to extend the spectral range.

In this work we test one of such applications – the use of ZnO NRs (in junction with a highly-resistive p-type silicon) as a sensitive photoresistor, however, the measured resistance is not resistance through the diode, but resistance of silicon which is a partner in the junction. The ZnO purpose is to improve the collection of light, broadening the depletion layer in Si and the creation of a conductive channel for photo-generated carriers (see Section 3). Surprisingly, the photoresistor response does not depend on gas environment and is fast. Thus, it cannot be related to surface processes, as commonly assumed. The slow decay process described in literature [11]

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http://dx.doi.org/10.1016/j.opelre.2017.02.001
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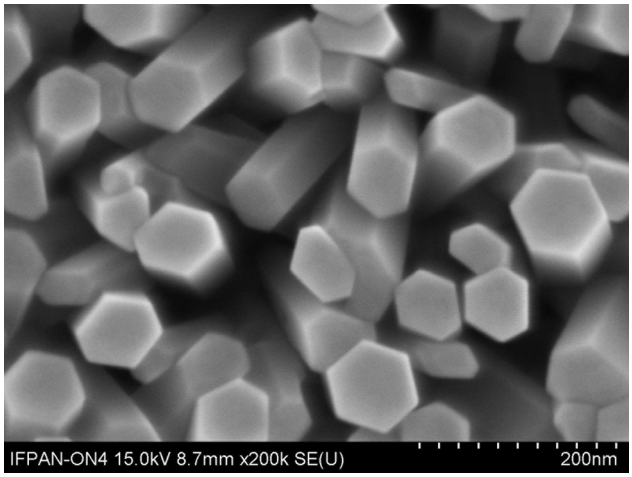

Fig. 1. Scanning electron microscope image of ZnO nanorods.

is not observed in this case. Nevertheless, the application of NRs is beneficial, since the response is much more sensitive than that of thin film ZnO/silicon junctions. (This statement is based on our investigations when we tested ZnO layers of different resistivity and thickness obtained by atomic layer deposition (ALD). Received responses were many times smaller.) Most probably, the use of NRs improves light collection as we reported recently for PV structures with ZnO NRs [4]. High quality and stoichiometry of ZnO NRs is also important for high sensitivity of the photodetector.

2. Experimental

Photoresistors investigated by us were prepared as follows. On a highly-resistive p-type silicon substrate (from Siegert Wafer GmbH, the measured acceptor concentration in silicon was of 1.6×10^{12} cm^{-3}) we deposited by ALD ZnO nanoseeds which nucleate the growth of ZnO NRs in the hydrothermal process. For seeds deposition it was enough to perform 10 ALD-cycles, with diethylzinc (DEZn) as a zinc precursor and deionized water as an oxygen precursor. The ALD process was performed at 100 °C in the ALD Savannah 100 reactor from Cambridge Nanotech. The so-prepared substrate with seeds was next placed inside of a microwave-assisted hydrothermal reactor (ERTEC Magnum II) together with a solution consisting of zinc acetate dissolved in deionized water. The pH value of the solution was equal to 8 (adjusted by a precipitation of a 1-mol solution of NaOH). The substrate and the solution were heated to approx. 50 °C and maintained at this temperature for approx. 1 min which was enough to grow ZnO NRs. Then, the substrate with ZnO NRs was rinsed with isopropanol and annealed in air for 10 min at 200 °C in order to clean the NRs surface from by-products of the reaction. Further details can be found in Ref. [12]. The SEM image of ZnO NRs produced in this way is shown in Fig. 1. NRs are disoriented (see Fig. 1) but are characterized by a very high crystallographic quality, as reported previously [12,17]. The nanorods are stoichiometric monocrystals without oxygen vacancies.

Next, Au ohmic contacts were deposited by sputtering on both sides of the sample (measuring surface: 5 mm × 5 mm). The measurement scheme is shown in Fig. 2.

The prepared sample was placed in a gas chamber with electrical outputs and a quartz window. A quartz lamp and a monochromator from the spectrometer SOLAR CM 2206 were used as a light source.

In the measurement configuration where the electric contact from gold fulfils the nanorods, we can achieve two parallel resistors (ZnO NWs matrix and silicon), but there is a huge difference in resistivity of silicon and NWs. Resistivity of the matrix of NWs is nearly

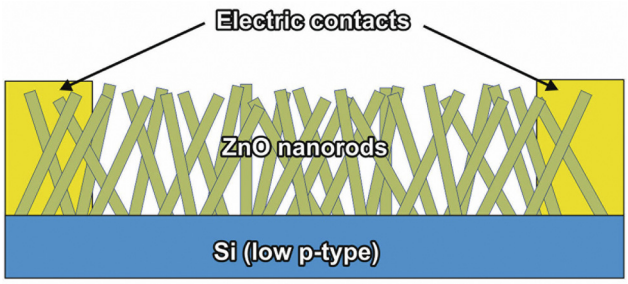

Fig. 2. Measurement scheme of the photoresistor.

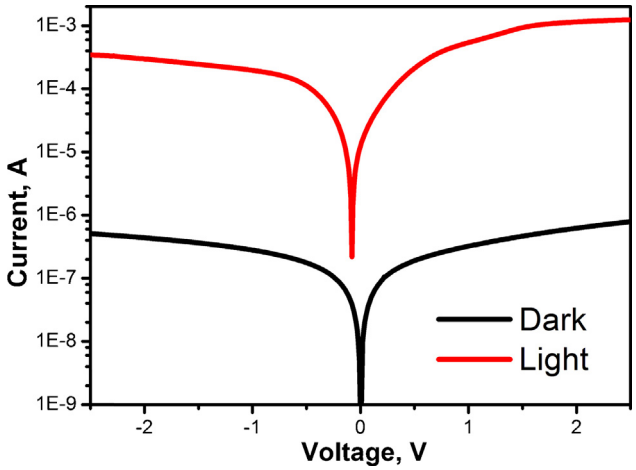

Fig. 3. I–V characteristics of the photoresistor.

thousand times higher than resistivity of a used silicon substrate, so the current through the NWs is negligible. During photo-electrical measurements we used light of a wavelength from the region of 400–1100 nm, so the light does not generates carriers in ZnO NWs.

Fig. 3 shows the I–V characteristics. The curve is similar to resistor characteristics. There are some perturbations for higher values of voltage, for the positive voltage current is slightly higher than in case of the same voltage in the opposite direction, but both dark and light characteristics are shifted in the same direction. It can be due to a problem with contacts. They can have slightly different sizes on the two sides of the sample and contacts were made “through” NWs which can form a barrier and slightly disturb the current flow.

The I–V characteristics were measured by using a Keithley 2601A multimeter. Resistivity of the sample were established using power supply by a GW INSTEK GDP-33036 set up for voltage of 1 V between contacts and Keithley 2206A as a current-metre (calculated later on resistivity of the sample).

3. Results and discussion

In the experiment resistance changes of the sample exposed to light of different wavelengths and to different gaseous environments were investigated. Exemplary results are shown in Fig. 4.

The observed response in the case of UV light (below 400 nm) is characterized by a fast resistance drop followed (after turning off the light) by a fast partial recovery and, then, a slow return to the initial resistance. The latter is typical for effects associated with surface reactions (such as cleaning of the surface from OH groups) as described in Ref. [11]. However, in the case of a sample illumination with light from the visible range we observe an entirely different response. A sharp decrease in resistance is observed upon illumination which returns to the baseline level immediately after the illumination is turned off. Importantly, this behaviour does not

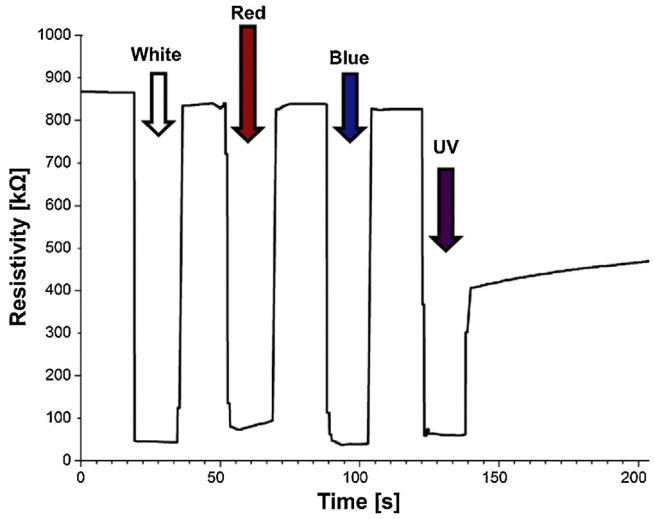

Fig. 4. Resistivity of the photoresistor under illumination at different wavelengths.

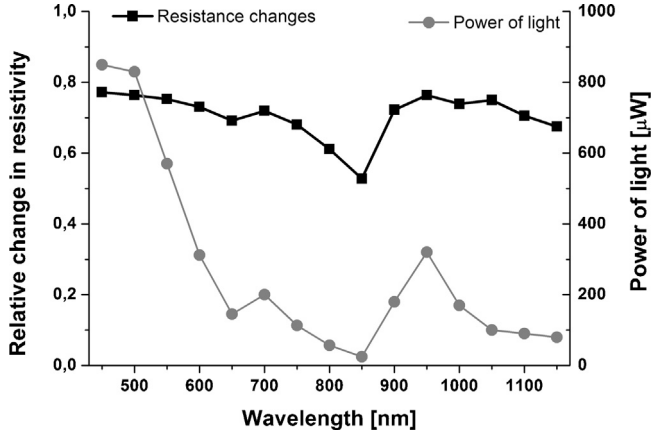

Fig. 5. Relative resistivity changes and applied light power as a function of wavelength.

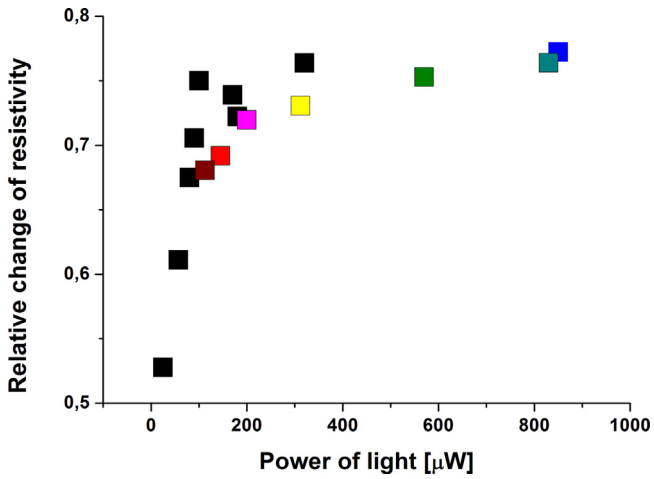

Fig. 6. Relative changes of the resistance as a function of light power. The experiment was performed in a wavelength region from 400 to 1100 nm. The colours of the markers are appropriate to the used wavelength of light (from violet to red), the black squares mean infrared region.

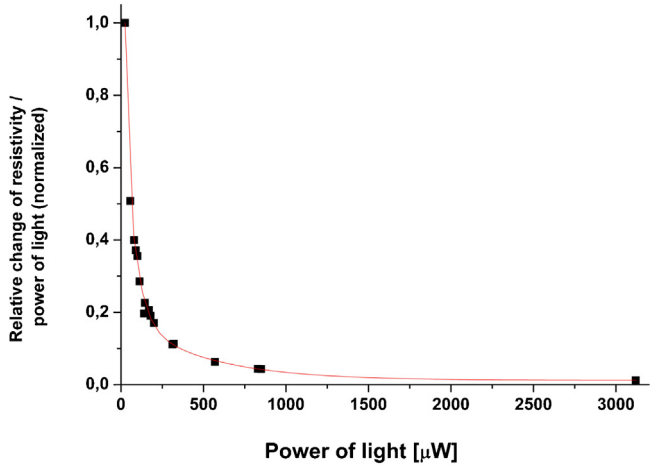

Fig. 7. Relative change in resistance divided by applied light power *vs.* light power.

depend on the gas environment (we tested the detector response in a chamber filled with oxygen, nitrogen, argon and at vacuum) which suggests a mechanism different from surface related processes.

The system exhibits a nonlinear type of dependence of resistance changes on light power, which was typically observed [13]. The relative changes in resistance depend very weakly on the power and wavelength of light, as shown in Fig. 5. This figure depicts the relative sensitivity ($\Delta R/R_0$, where R_0 is the resistivity in the dark) and the power of light applied at different wavelengths.

Despite the relatively large differences in light power, the detector sensitivity hardly changes (as a function of wavelength) only slightly reflecting the fluctuations in the excitation power. Fig. 6 shows the sensitivity ($\Delta R/R_0$) as a function of light power at a constant wavelength. At low light powers the detector sensitivity grows rapidly, but above 100 μW the response nearly saturates. Then, even a large change in the light power causes only a slight change in the system response. Whereas, for a very small light intensity (20 μW) a relative change in resistance is over 50%, for a 10 times greater light power the relative change in the resistance is only slightly higher than 70%. A further increase of the excitation power only slightly increases the detector response.

This relation is better illustrated in Fig. 7, showing the relative change in resistance divided by the applied light power (over the range 400–1150 nm) as a function of light power.

Fig. 7 shows the hyperbolic decay in sensitivity with increasing power of light. This type of response to visible light is not related to the chemical environment or photoconductivity, but depends on the band structure of the Si-ZnO junction, as explained below.

To explain such a mechanism of photoresponse, we calculated the energy band diagram based on Anderson's model [18]. The electron affinity and band gap values for ZnO are $\chi = 4.35$ eV and $E_g = 3.37$ eV, respectively [19,20]. For silicon χ and E_g values are $\chi = 4.05$ eV and $E_g = 1.12$ eV, respectively [20]. The Anderson's model gives a small conduction band offset which equals 0.3 eV ($\Delta E_C = \chi_{ZnO} - \chi_{Si}$) and a large valence band offset equal to 2.55 eV ($\Delta E_V = E_{gZnO} - E_{gSi} + \Delta E_C$) [20,21].

To determine the built-in potential (V_{bi}) and the width of the depletion region (x), we took the acceptor concentration in silicon equal to 1.5×10^{12} cm^{-3}. The donor concentration in ZnO was calculated from the slope of $1/C^2$ to be 2.2×10^{15} cm^{-3}. The value of the built-in potential was determined from Fig. 8. The measured value of the built-in potential is of 1.75 V.

Based on the Anderson model, the energy band diagram was calculated for the n-ZnO/p-Si heterojunction, as shown in Fig. 9. Calculations show that almost the whole depletion region is on the silicon side ($x_2 = 25$ μm). On the ZnO side the width of the depletion region is only 17 nm. This means that the carriers are generated predominantly on the silicon side of the junction. They are subse-

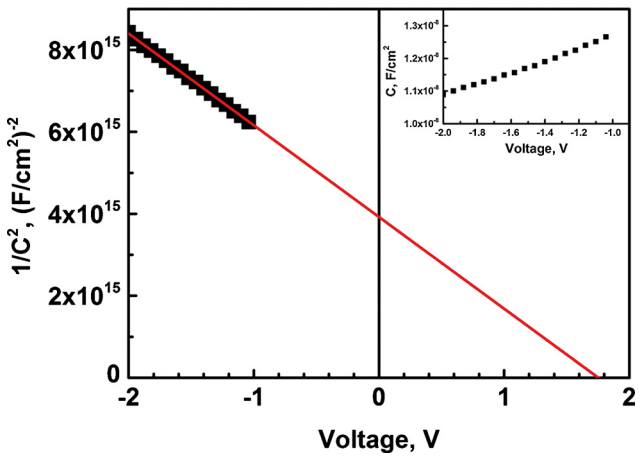

Fig. 8. Capacitance–voltage characteristics of the ZnO NR/Si heterojunction. The intercept of the red line with the voltage axis determines the value of the built-in potential.

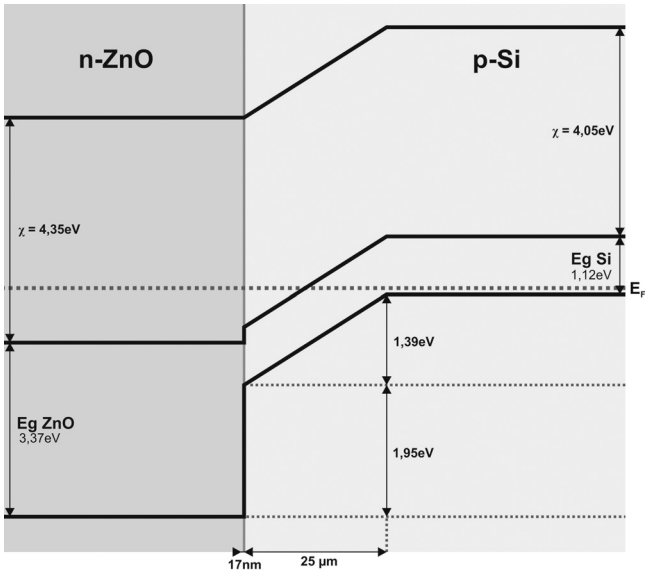

Fig. 9. Band diagram of the ZnO/Si heterojunction.

quently separated by the built-in potential and diffuse into ZnO and, then, to the electrodes.

Based on the calculations we can explain the mechanism of light detection. The absorption of light near the junction of two materials causes generation of electron-hole pairs which are separated by the band bending in the depletion layer. The band bending causes the flow of electrons to ZnO NRs (slightly n-type) which are not actively involved in the photo-current. The holes gather on the Si side, thus, creating an active conducting channel. The depletion layer on the Si side is 25 μm thick (!), so the separation area is very large. A higher intensity of light results in generation of a larger number of carriers, but along with the increase of hole concentration in Si, the width of the depletion layer decreases. The latter will decrease the carrier separation and, thus, the detector's response. Therefore, for very low light intensities (a few μW) the detector sensitivity is very high, but at an increased light power the system response starts to saturate.

4. Conclusions

The photoresistor based on ZnO NRs and silicon substrate developed by us is characterized by high sensitivity at low light intensities, and by a quite uncommon detection mechanism. The wavelength detection range is between 400 and 1100 nm which reflects light absorption by the silicon partner of the junction. Importantly, post-illumination annealing or chemical treatment is not necessary before the detector's reuse. High sensitivity and the extremely simple manufacturing technology make this detector very attractive for potential applications. Poor relationship between the response and the light intensity enables usage as an optical switch.

Acknowledgements

The research was financially supported by the National Science Centre through the grant no. (DEC-2012/07/N/ST3/03144).

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