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

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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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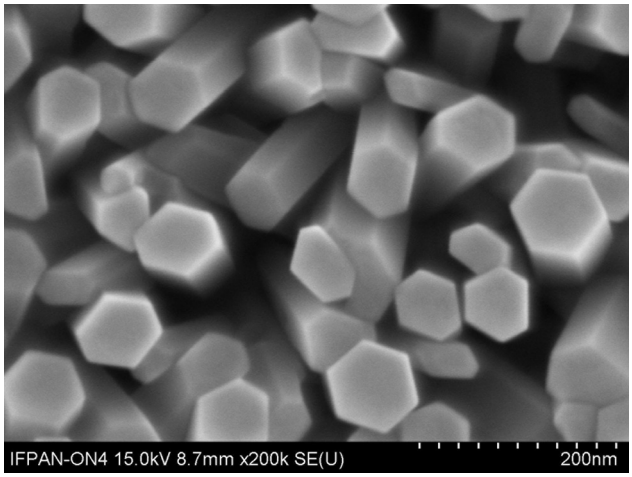

Fig. 1. Scanning electron microscope image of ZnO nanorods.

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

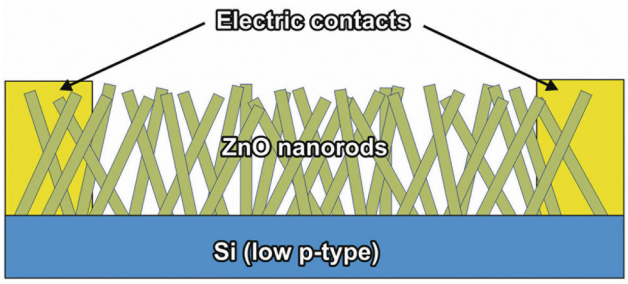

Fig. 2. Measurement scheme of the photoresistor.

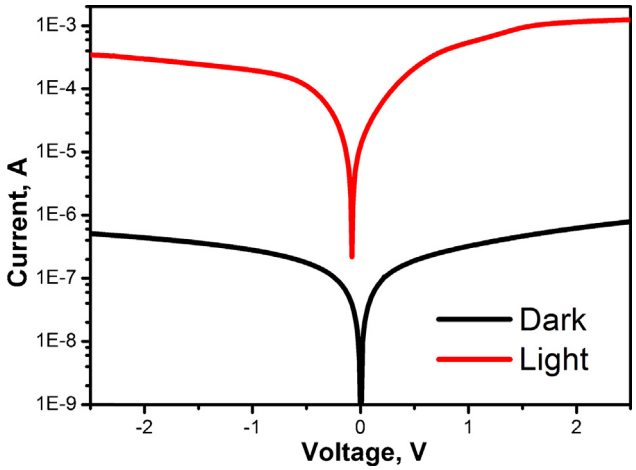

Fig. 3. I–V characteristics of the photoresistor.

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