Photoelectric properties of MSM structure based on ZnO nanorods, received by thermal evaporation and carbothermal synthesis.

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Abstract. Photoelectric characteristics of metal-semiconductor-metal (MSM) structures: Au/ZnO(nanorods)/ZnO(film)/ZnO(nanorods)/Au were investigated. Synthesis of ZnO nanorods (NR's) was carried out by two different methods, such as catalyst-free carbothermal synthesis (t = 950°C, precursor - ZnO:C) and catalyst-free thermal evaporation of metallic Zn (t = 600°C, precursor Zn). Photoluminescence spectra have shown that the ZnO NR's obtained by means of thermal evaporation technique have a lower concentration of point defects related with oxygen vacancies, than ZnO NR's prepared by carbothermal synthesis. MSM structure with ZnO NR's obtained by thermal evaporation technique have photosensitivity 97 mA/W at ~ 325 nm illumination and 44 mA/W at ~ 518 nm illumination at a bias 5V. For MSM structure with ZnO NR's obtained by method of carbothermal synthesis, the photosensitivity values were 22 mA/W, and 103 mA/W, respectively.

1. Introduction

Recently, interest to a one-dimensional ZnO nanostructures for fundamental research has increased due to their specific characteristics, such as the dimensional quantum effects and large surface area of zinc oxide nanostructures. Also, there is a huge potential for the use of such structures in nanoelectronics [1, 2]. Furthermore ZnO has several special properties: high adsorption capacity, radiation resistance, transparency in the visible range of the electromagnetic radiation and direct wide band gap (3.37 eV) [3, 4]. ZnO can form a Schottky barrier with metals such as Pt and Au [5], and as is known, such photodiode structures have higher performance than the conventional p-n junction. All of these properties are very attractive for creation high performance photosensitive structure based on Schottky barrier Au/ZnO, and operating in the ultraviolet (UV) spectrum.

The main aim of this work was studying of the photovoltaic curves of metal-semiconductor-metal (MSM) structure: Au/ZnO(NR's)/ZnO(film)/ZnO(NR's)/Au. These photodetectors can be used in areas where the control of UV radiation is needs, for example, to monitor solar radiation, UV radiation in air and water disinfection systems.
2. Experiment

MSM structures were produced on the Si (100) substrate with thin oxide layer SiO$_2$. Deposition of ZnO thin film was carried out by pulsed laser deposition (PLD) in an oxygen atmosphere, P(O$_2$) = 2×10$^{-2}$ mbar at a substrate temperature of 500°C, the distance between the target and the substrate was 50 mm. For the ablation of ZnO target was used KrF-excimer laser with wavelength of 248 nm and frequency f = 10 Hz. The flux density of the laser pulse energy was ~ 2.3 J/cm$^2$. ZnO film used as a sublayer reducing the barrier nucleation during the growth of nanorods ZnO. ZnO nanorods growth was carried out by two different methods: catalyst-free vapor phase transport growth (thermal evaporation of metallic Zn) and catalyst-free carbothermal synthesis. In the vapor phase transport synthesis [6], evaporation of zinc produced in the argon and oxygen atmosphere at 600°C. The argon flow was 240 sccm, oxygen flow was 8 sccm and synthesis pressure was 15 mbar (scheme of the reaction chamber shown in Fig. 1a). In the carbothermal synthesis (scheme of the reaction chamber shown in Fig. 1b) [7, 8] was used pressed tablet of ZnO and C as a precursor (1:1 on the molar mass). The synthesis temperature was 950°C. The argon flow is 200 sccm and synthesis pressure is 20 mbar.

![Fig. 1](Schematic illustration of the reaction chambers: a) - catalyst-free vapor phase transport growth (in this case Zn precursor is located in the center of a quartz tube, which is open on both sides) and b) - catalyst-free carbothermal synthesis (it uses a quartz tube with one closed (soldered) end).

After the synthesis of ZnO nanorods, Au contacts were deposited on the nanorods surface through a mask by PLD at room temperature under vacuum value 2×10$^{-5}$ mbar, a distance between the target and the substrate was 50 mm, the laser wavelength $\lambda = 248$ nm, frequency $f = 10$ Hz, the energy density was 3.7 J/cm$^2$. During the deposition structure was located at 45° to the axis of the plasma torch, for uniform deposition of gold on the surface of the nanorods ZnO. Thus was obtained a structure based on a double Schottky barrier: Au/ZnO(NR’s)/ZnO(film)/ZnO(NR’s)/Au (Fig. 2).

![Fig. 2](Schematic view of the MSM structure.)

3. Experimental results and discussion

The main difference between two techniques is a lower temperature of synthesis at vapor phase transport method (600°C) than at the carbothermal synthesis (950°C), resulting in a lower defect concentration in ZnO NR’s [9]. This fact is proved by photoluminescence spectra (Fig. 3), which show that the ZnO NR’s produced by vapor phase transport synthesis have a high peak in the UV region of the spectrum with a peak wavelength of ~ 380 nm, and low peak in the green region of the spectrum, at wavelength ~ 525 nm (Fig. 3a). This fact can indicate low concentration of point defects related with oxygen vacancies in samples. Opposite situation is observed for ZnO nanorods, obtained by carbothermal method. (Fig. 3b).
Fig. 3. Photoluminescence spectra of ZnO NR’s, obtained a) - catalyst-free vapor phase transport growth and b) - catalyst-free carbothermal synthesis.

I-U curves (Fig. 4a, 4b) of MSM photodetectors (Au/ZnO(NR’s)/ZnO(film)/ZnO(NR’s)/Au) shows that studied structures have sensitivity in the visible and ultraviolet region of the spectrum. MSM structure with ZnO NR's prepared by the method of thermal evaporation, has a high photosensitivity in the ultraviolet region of the spectrum (~ 325 nm) - 97 mA/W, and low photosensitivity in the green region (~ 518 nm) - 44 mA/W (Fig. 4b). For structures prepared by carbothermal synthesis photosensitivity values were 22 mA/W and 103 mA/W respectively at a bias 5V (Fig. 4a). It is caused by low concentration of defects in ZnO NR’s produced by vapor phase transport synthesis.

Fig. 4. I-U curves of MSM structure: a) – ZnO NR’s produced by carbothermal method; b) – ZnO NR’s produced by thermal evaporation.
Bandgap of ZnO is 3.37 eV (corresponding to the energy of photons with a wavelength ~ 375 nm), and hence the sensitivity at a wavelength of ~ 325 nm is easily explained by the intrinsic absorption of ZnO. Thus photons have a higher energy than the band gap of a semiconductor, so the optical excitation occurs from the valence band to the conduction band. Then charge separation occurs at the Schottky barrier. In addition, these structures have a photosensitivity in the visible region of the spectrum, as seen from Fig. 4a and 4b. This is due to the presence of point defects related with oxygen vacancies in ZnO. So, if the donor defect levels are in the band gap of ZnO, then electron transfer between these levels and bands requires minimal energy. In this case the generation of charge carriers will occur even when excited by light with photon energies below the band gap of zinc oxide.

The temporal response (Fig. 5) of MSM structure for ZnO NR’s, produced by the method of thermal evaporation, was received by laser pulses excitation with 10 ns pulse length (Nd-YAG laser, \( \lambda = 355 \text{ nm} \)) at a bias 5V. Rise time was ~ 1 \( \mu \text{s} \). The fall time at full-width at half-maximum was ~ 10 \( \mu \text{s} \).

**Fig. 5.** a) - temporal response of MSM detectors based ZnO NR’s excited by Nd-YAG laser (\( \lambda = 355 \text{ nm} \), 10 ns).

Due to good radiation durability, high photosensitivity and performance our photodetectors could find wide application in many areas where the control of UV radiation needs, for example, to monitor the UV solar radiation, UV radiation monitoring in air and water disinfection devices, etc [10].

**References**

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