Facile fabrication of a TiO_2 NW-base glucose sensor by direct ink writing

A. Tarasov[1], S. Dubkov[1], D. Gromov[1], R. Ryazanov[2], L. Volkova[3]

[1]National Research University Moscow Institute of Electronic Technology, Russia, Zelenograd
[2]Scientific-Manufactoring Complex "Technological Center",Russia, Zelenograd
[3]Institute of Nanotechnology of Microelectronics RAS,Moscow, Russia
e-mail: bloggger4@gmail.com, tel: +7(901)779-35-00

About this work

In this work, it is proposed to obtain a biosensor based on layers of TiO_2 nanowires. The sensitive layer was formed by direct ink writing (DIW) on a silicon wafer with an oxide layer on the surface. The synthesis of nanowires is carried out by the hydrothermal method in an alkaline solution. This method makes it easy to control the morphology of nanowires. Nanonites with an average density of about 8 μm were found. Annealing changed the changing composition of the nanowires. Gold contacts on a silicon wafer were formed by vacuum thermal evaporation. Functional layers were printed from an allergic compound. The performed measurements of the current-voltage characteristics of the sensitivity showed an increase in the current upon detection of a target in a solution, which indicates the presence of sensory properties of the income layers.

Experimental

The synthesis of TiO_2 nanowires were carried out by hydrothermal method. For synthesis, 0.3 g of commercial TiO_2 powder (P25 Evonik) and 50 mL of 10 M NaOH aqueous solution were putted into a Teflon-lined stainless autoclave and heated. Fill factor 1/2. After synthesis, the nanowires were washed in a 0.1 M HCl solution to neutralize alkali residues and Na ions. Then it is necessary to remove the remaining acid by washing in deionized water with constant stirring and heating. The nanofilaments were filtered and added to water again. Washing was carried out up to normal pH = 7. The synthesis temperature was constant and amounted to 250 °C. Synthesis time 3, 6, 9 and 12 hours. Then, the dependence of the synthesis temperature on the nanowire morphology was studied. The synthesis was carried out for 12 hours at temperatures of 150 and 200 °C.

To study the effect of thermal post-treatment on the crystal structure of titanium dioxide nanowires, annealing was carried out. Annealing was carried out in air for 4 hours at temperatures of 500, 700, and 900 °C.

For the formation of sensitive elements of the glucose sensor by direct printing, two inks were prepared. The first option was based on an aqueous suspension. 20 mg of TiO_2 nanowires were added to 20 ml of deionized water, and ultrasonic treatment was carried out. The second version of the ink was based on an aqueous solution of polyvinyl alcohol (PVA). PVA (20 g) was added to 20 ml of deionized water, stirred until complete dissolution, 20 mg of TiO_2 nanowires were added, and the ink was sonicated.

The contacts were formatted by vacuum-thermal evaporation of Au on silicon surface with SiO_2 layer. Size of the contacts were 2*2 mm, 100 nm thick and 5 mm apart.

The formation of sensitive elements of the sensor by the direct ink writing (DIW) method was carried out on a modified 3D printer with a specially designed print head, inside which a syringe with ink is fixed. Nozzle diameter 0.4 mm, heated table temperature 100°C. When using inks with polymer, subsequent heat treatment is necessary to burn out the polymer. Burning was carried out in air at a temperature of 600 °C for 10 minutes

The study of the sensory properties of titanium dioxide nanowires was carried out by measuring the current-voltage characteristics of the sensitive layer coated with 10 µl of 5, 10, and 100 µM glucose solution. An agilent e3647a power supply, a keithley 6485 picoampimeter, a keithley 2700 multimeter, and a probe station were used for measurements.

TiO_2 nanowires

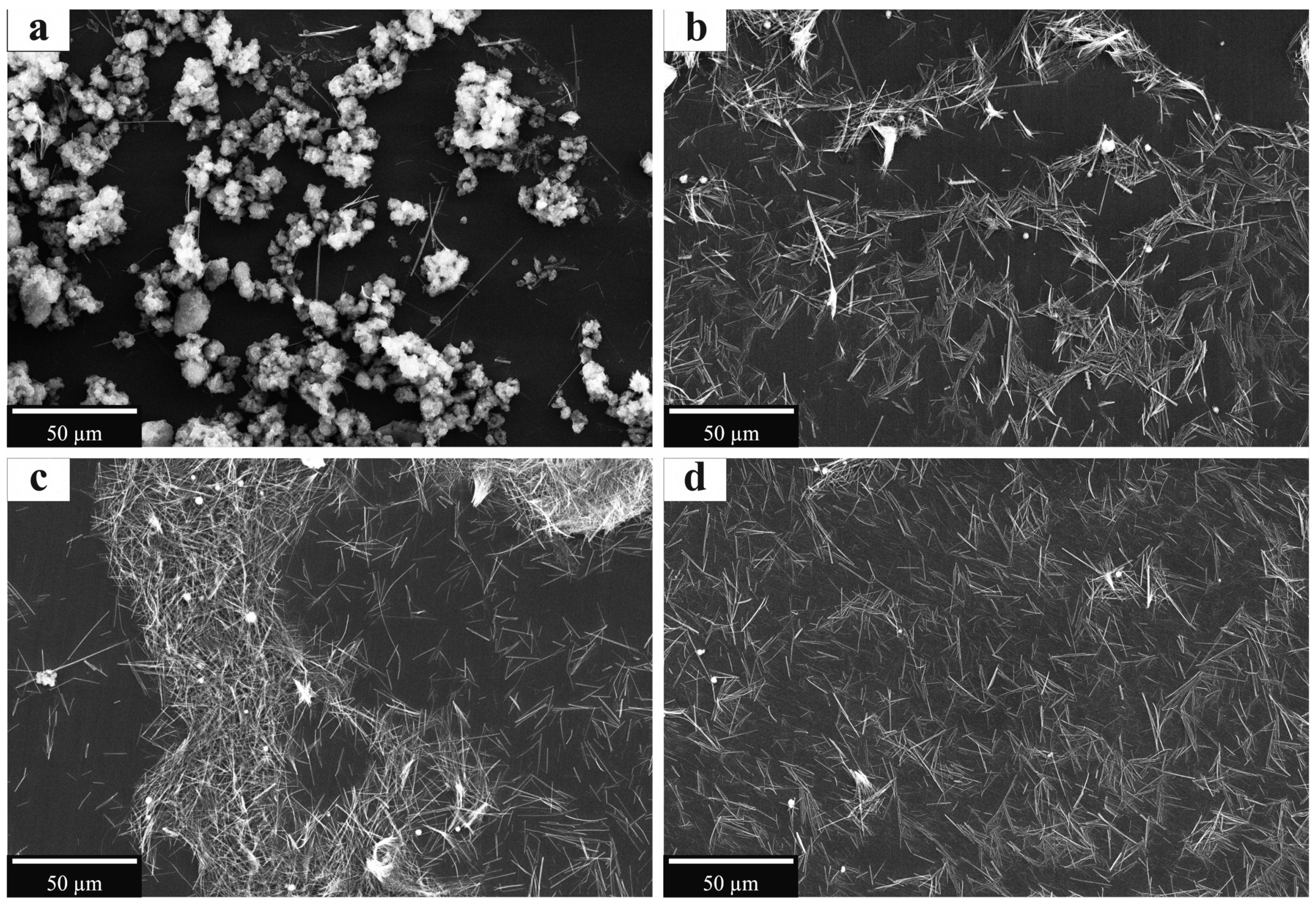

Figure 1 – SEM images of nanowires after (a) 3, (b) 6, (c) 9 and (e) 12 hours synthesis at 250 °C

First, the effect of synthesis time on the morphology of TiO_2 nanowires was studied. The image Fig. 1 shows SEM images of nanowires at different synthesis times. After three hours of synthesis (Fig. 1a), single nanowires formations and large agglomerates are observed. As the synthesis time increases, the number of agglomerates decreases and reaches its minimum after 12 hours (Fig. 1d). Therefore, a 12-hour synthesis with an average nanowires length of 8 µm was chosen as the most optimal one.

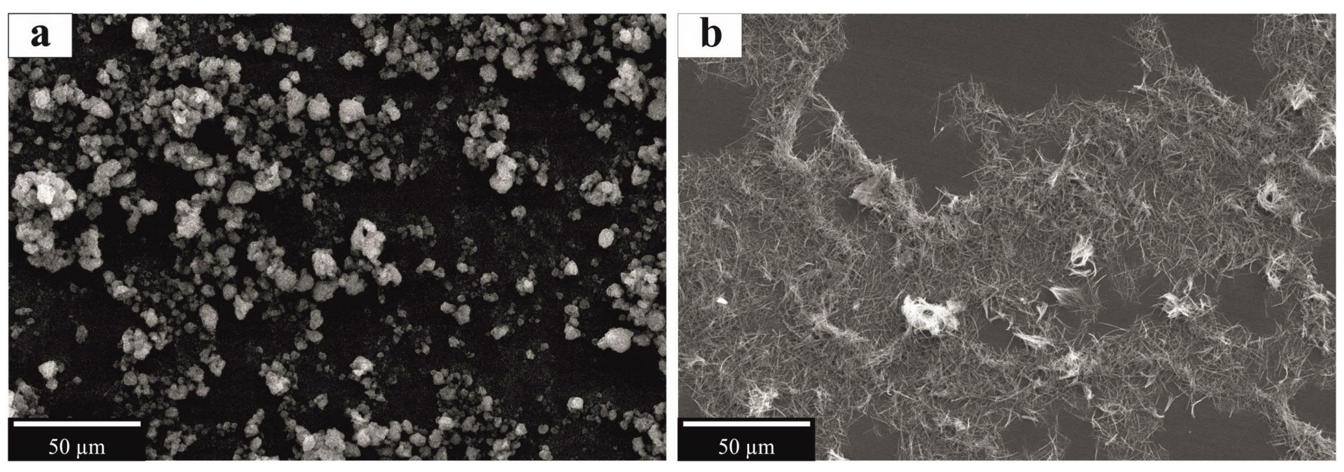

Figure 2 – SEM images of nanowires synthesis at (a) 150 °C and (b) 200 °C for 12 hours

The image Fig. 2 shows SEM images of nanowires at different temperatures. At 150 °C (Fig. 2a), no growth of nanowires is observed. At 200 °C, the average length of nanowires was 4 µm, which is two times less than in synthesis at 250 °C. Therefore, a synthesis mode of 250 °C and 12 hours was chosen.

After synthesis, nanowires do not have crystallinity. To obtain a specific crystalline phase, it is necessary to carry out thermal post-processing. Fig. 3 shows the spectrum at various post-processing temperatures. At 500 °C, mainly anatase and TiO_2-B peaks are observed. After annealing at 700 °C, peaks characteristic of rutile appears. Rutile peaks dominate after annealing at 900 °C. It is believed that the highest catalytic activity is observed in samples that are an anatase-rutile mixture. Therefore, annealing at 700 °C was chosen for further work.

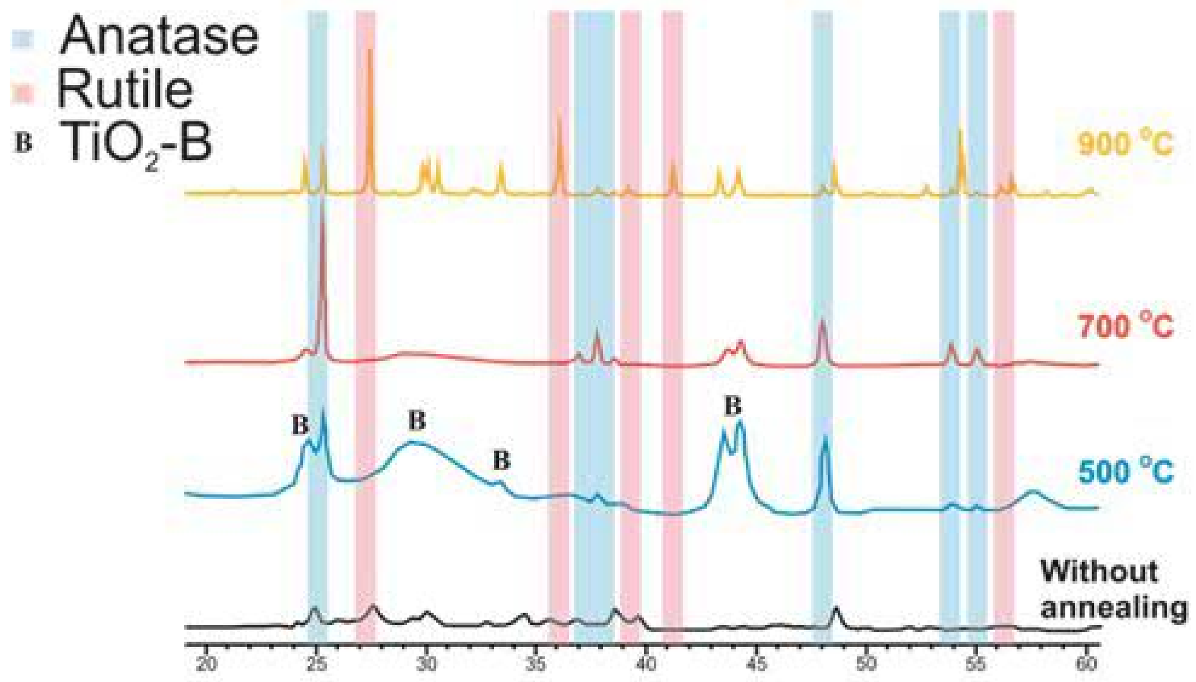

Figure 3 – X-ray structural analysis of heat treated in air for 4 hours at ambient temperature.

Printing of sensitive layers

When printing with water-based ink, a non-continuous layer is formed. This can be explained by the low viscosity of such inks. The use of ink based on PVA water solution gives the best result. The image Fig. 4 shows SEM images of layers of TiO_2 nanowires formed by the DIW method. When printing with water-based ink (Fig. 4 a), a non-continuous layer is formed. This can be explained by the low viscosity of such inks. The use of ink based on PVA water solution gives the best result (Fig.4 b).

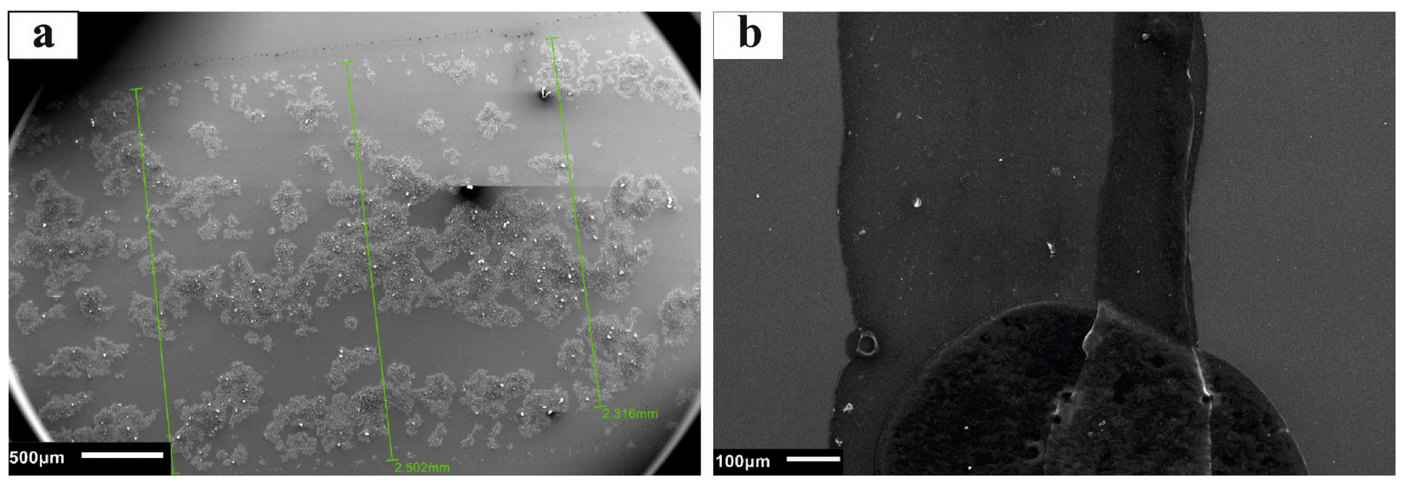

Figure 4 – SEM images of printed layers based on TiO2 nanowires (a) water ink and (b) aqueous solution PVA (before annealing).

After annealing, only nanowires remain on the silicon wafer surface. These nanofilaments have a preferred direction. The direction is the same as the movement of the print head. This effect can affect the sensitivity of the sensor.

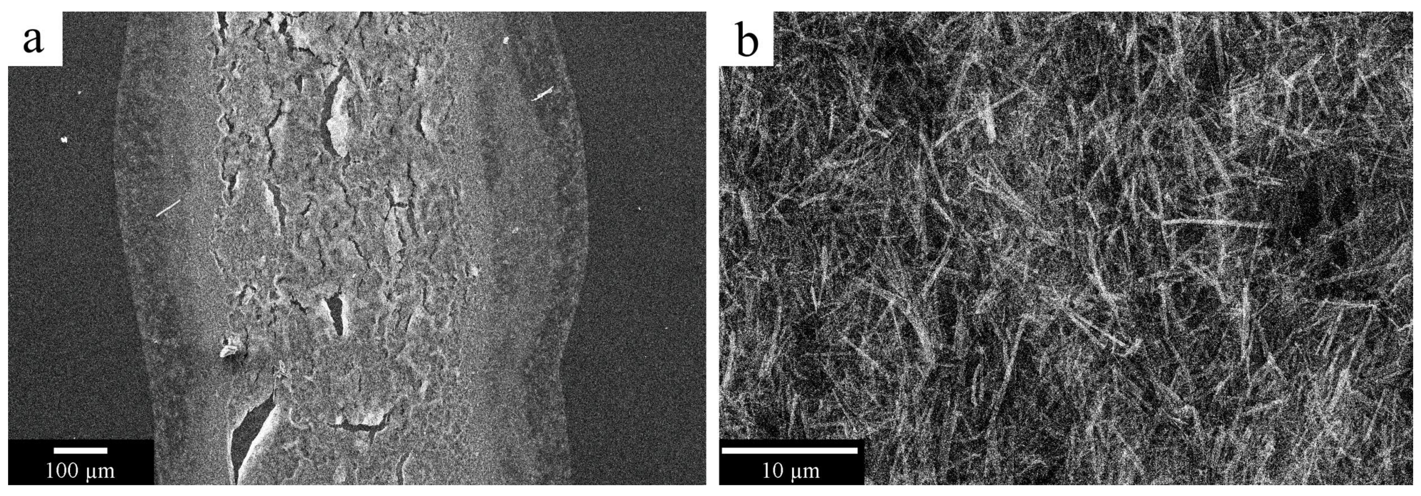

Figure 4 – SEM images of printed layers based on TiO2 nanowires (a) water ink and (b) aqueous solution PVA (before annealing).

After annealing, only nanowires remain on the silicon wafer surface. These nanofilaments have a preferred direction. The direction is the same as the movement of the print head. This effect can affect the sensitivity of the sensor.

The obtained current-voltage characteristics (Fig. 5) demonstrate the sensitivity of the sensor to low concentrations of glucose. With an increase in glucose concentration, the conductivity of the sensitive layer increases.

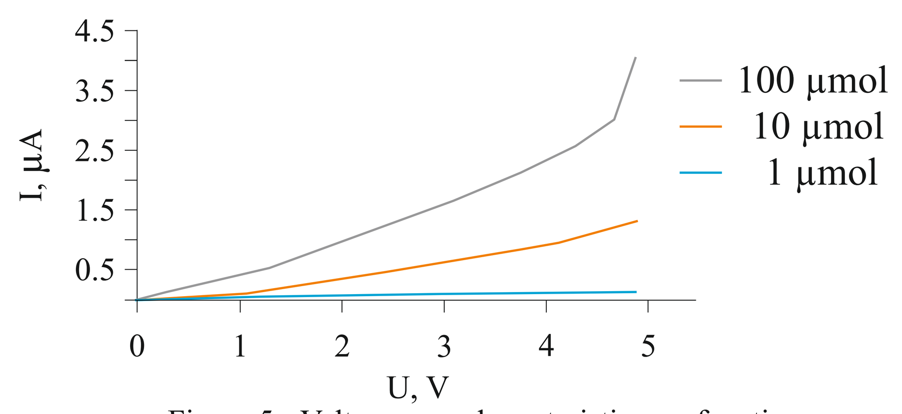

Figure 5 - Volt-ampere characteristic as a function of glucose concentration

Conclusion

In this work, a facile synthesis of TiO2 nanowires was demonstrated. The average length of nanowires was 6, 7 and 8 µm for 6, 9 and 12 hours of synthesis for 250 °C. The dependences of the crystal structure on the annealing temperature were obtained. Anatase is formed after annealing at 500 °C, a mixture of rutile anatase at 700 °C and rutile at 900 °C. The obtained ink showed that viscosity is an important parameter for DIW printing. This was demonstrated using two suspensions as an example. A more viscous PVA aqueous solution showed better layer morphology. Based on such ink, a glucose sensor was created. The sensor showed sensitivity to micromolar concentrations of glucose solution.

ASCO-NANOMAT 2022, Vladivostok, Russia

Thank you for your interest in our work.
Please send an email, I will be glad to answer.
Thanks to the organizers of the conference.

amt-miet.ru