# UV selective photodetector based on nanosized TiO<sub>2</sub> layers

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Nanosized TiO<sub>2</sub> layers were obtained by conventional vacuum thermal evaporation of Ti and triode-cathode sputtering of Ti target in a vacuum system on silicon and quartz substrates, with high temperature post annealing to TiO<sub>2</sub> in the range of  $(450 \div 750)^{\circ}$ C. Structures for UV sensors are formed by contact thermal evaporation of combing contact Al, Ni, In and In-Sn on TiO<sub>2</sub> layers of silicon substrates. The optical properties of TiO<sub>2</sub> were studied by measuring the transmittance spectra in the range of wavelengths (200÷900) nm.

Spectral characteristics of structures with Al and Ni contacts show a maximum spectral sensitivity in the range of  $(280 \div 330)$  nm. I-V characteristics are measured at  $4 \div 30$  V forward voltage in the dark and under illumination with blue LED (380 nm) and with an Hg lamp 50 W (365 nm). Under Hg lamp illumination, and  $(6 \div 10)$  V bias voltage, photocurrent increases of magnitude, which shows that the structure of Al and Ni contacts are suitable for UV sensors.

Key words: titanium dioxide, UV sensors, I-V characteristics, spectral characteristics

#### INTRODUCTION

The need of monitoring the UV radiation led to the development of the UV sensors based on different materials. TiO<sub>2</sub> is one of the most attractive metal oxides as a cheap, safe, simple and chemically stable material. Absorption of UV light by TiO<sub>2</sub> is widely applied when used as a photocatalyst, but the process of light absorption of TiO<sub>2</sub> and occurrence of photocurrent, hard work recent years, because the characteristics of TiO<sub>2</sub> photodiodes make them suitable for the detection of UV radiation.

Due to the band gap of  $TiO_2$  (3.0 eV for rutile and 3.2 eV for anatase), it is generally sensitive to UV radiation and do not require UV filters unlike silicon UV photodiodes. Studies in the literature show that the TiO<sub>2</sub> can be used for UV and other types of sensors, due to a distinct characteristic absorption, high sensitivity and resolution, and possibility traditional silicon to be used as a substrate.

### EXPERIMENTAL

TiO<sub>2</sub> was prepared by two methods: conventional vacuum thermal evaporation of Ti layer and sputtering of Ti target in a cathode-triode vacuum system in argon flow  $(2 \div 6) \times 10^{-3}$  mbar with a preliminary ion scrubbing. The substrates are optical quartz, sital and silicon at temperatures up to 100°C. In both methods, TiO<sub>2</sub> is formed by high-temperature annealing of the titanium layer into a resistance furnace on air at

temperatures  $T_{\rm ann} \approx 450,600$  and  $700^{\circ}$ C for  $1\div 5$  h. The layers have a thickness of  $100\div 300$  nm, have a regular surface in both the method of preparation, such as the adhesion is improved with increasing annealing temperature. It is believed that at  $T_{\rm ann} \approx 450^{\circ}$ C anatase phase is formed, at  $T_{\rm ann} > 450^{\circ}$ C both phases anatase/rutile are formed, and  $T_{\rm ann} > 650^{\circ}$ C formed rutile [1,2].

The optical properties of  $TiO_2$  were analyzed using the spectra of transmittance. The spectral characteristics of the transition are measured with a spectrophotometer UV-VIS SPECTROMOM 195D within a range of wavelengths of 200÷900 nm. The spectra are dependent on the substrate temperature, the layer thickness and the temperature of annealing.

The width of the band gap energy for direct and indirect transitions was obtained by plotting the optical absorption  $(\alpha hv)^2$  and  $(\alpha hv)^{1/2}$  vs. photon energy (hv) and extrapolating the linear portion of the curve to 0 [3]. Values obtained for the width of the band gap in the two used methods: thermal evaporation and cathode-triode sputtering correspond to TiO<sub>2</sub> anatase crystalline phase at annealing 450°C and predominant presence of rutile TiO<sub>2</sub> crystalline phase at temperatures from 600 to 750°C.

For the preparation of structures sensitive to UV radiation nanosized TiO<sub>2</sub> layers with thicknesses in the range of  $90 \div 280$  nm are formed on n-Si (100) wafers with a specific resistance (6÷9)  $\Omega$ .cm. After that using a variety of metals such as Al, Ni, In and In-Sn on the layers are designed electrodes by thermal evaporation through a contact mask. The realized structures having a meander shape are mounted on

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Fig. 1. Photograph (a) and I-V characteristic (b) of a structure n-Si/TiO<sub>2</sub>/Al.

golden packages with conductive Ag paste. Fig. 1(a) presents a photograph of structure Si/TiO<sub>2</sub>/Al.

## RESULTS

I-V characteristics of the structures were measured in the range  $4\div30$  V in the dark, illuminated with blue LED (wavelength  $\lambda = 380$  nm) and illuminated with an Hg lamp 50 W (with filter for radiation with  $\lambda = 365$  nm). Best results when illuminated with both lengths  $\lambda$ , are obtained from the structures with Ni and Al contacts (n-Si/TiO<sub>2</sub>/Ni and n-Si/TiO<sub>2</sub>/Al).

Fig. 1(b) presents I-V characteristics of pattern 19(2) – structure Si/TiO<sub>2</sub>/Al with thickness of TiO<sub>2</sub> – 90 nm and Al contacts. When the applied voltage

10 V, the dark current increased from 56  $\mu$ A to photocurrent of 700  $\mu$ A after illumination with Hg lamp, i.e. photocurrent increased one order of magnitude in comparison with the dark current.

The photocurrent depends on the thickness of  $TiO_2$  layer. On the one side for thicker layers generation of carriers grows, but on the other it accelerates their recombination and photocurrent increase is slowing. Increasing of the bias voltage applied to the structure also slows the growth of photocurrent.

In Fig. 2 (a) and (b) are shown I-V characteristics of patterns 19 (3) and 51 with thicknesses 140 and 170 nm respectively and with Ni contacts, measured in the range of  $(4\div 30)$  V. The best results for the photocurrent versus dark current was obtained in



Fig. 2. I-V characteristics of structures n-Si/TiO<sub>2</sub>/Ni - patterns 19 (3) (a) and 51 (b).



Fig. 3. Spectral characteristics of structures with Al (a) and Ni (b) contacts.

layers with thicknesses  $90 \div 170$  nm and at applied bias voltage in the range of  $(6 \div 12)$  V.

The spectral characteristics of the photocurrent of the structures with Al and Ni contacts are shown in Fig. 3. They show low dependence on the applied to the structure bias voltage and have photosensitivity in the range of  $280 \div 330$  nm, which is in good agreement with the results of the absorption spectra.

Fig. 4 presents the spectra of transmittance and absorption of a sample 19(2), which show a strong optical absorption in the range  $250 \div 320$  nm.

The width of the optical zone of direct and indirect transitions is obtained from a graphs of the optical ab-

sorption  $(\alpha hv)^2$  and  $(\alpha hv)^{1/2}$  vs. photon energy (hv)and linear extrapolation to 0. The width of the optical zone of direct transitions of TiO<sub>2</sub> is determined 3.4 eV at annealing temperature 450°C and 3.2 eV with increasing annealing temperature up to 600°C. The width of the optical zone of indirect transitions is 3.12 eV at annealing temperature 450°C and 3.02 eV with increasing annealing temperature up to 750°C.

## CONCLUSIONS

In most published literature values for the width of the optical zone of  $TiO_2$  – anatase and rutile, respectively, are in the range  $3.0 \div 3.4$  eV, i.e. within a range



Fig. 4. Optical absorption in TiO<sub>2</sub> thin films.

of wavelengths of  $370 \div 420$  nm. Values obtained for the energy of the direct and indirect transitions correspond to TiO<sub>2</sub> anatase crystalline phase at annealing temperatures of  $450^{\circ}$ C and with increasing annealing temperature up to  $750^{\circ}$ C showed mostly presence of rutile crystal phase. Changes in the width of the optical zone with annealing temperature are related to changes in the dimensions of the crystallites, as well as varying the ratio between the crystalline phase of anatase and rutile [2].

I-V characteristics show good current differences between the dark current and photocurrent when illuminated by UV radiation. Half-width of the spectral characteristics showed good sensitivity range of  $235 \div 420$  nm. At applied bias voltage in the range of  $6 \div 10$  V photocurrent increased one order of magnitude in comparison with the dark current.

These results suggest that the structures and n-Si/TiO<sub>2</sub>/Ni n-Si/TiO<sub>2</sub>/Al are suitable for UV sensors.

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## UV СЕНЗОРИ НА ОСНОВАТА НА ТІО<sub>2</sub> Л. Бедикян, Ст. Захариев, М. Захариева

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#### (Резюме)

Наноразмерни слоеве TiO<sub>2</sub> са получени чрез стандартно вакуумно термично изпарение на Ti и триодно-катодно разпрашване на Ti мишена във вакуумна система върху силициеви и кварцови подложки, с последващо високотемпературно окисление до TiO<sub>2</sub> при  $450 \div 750^{\circ}$ C. Структурите за UV сензори са формирани чрез контактно термично изпарение на гребеновидни контакти Al, Ni, In и In-Sn върху слоевете TiO<sub>2</sub>/Si. Оптичните свойства на TiO<sub>2</sub> са изследвани чрез измерване спектрите на пропускане в интервал от дължини на вълната 200÷900 nm.

Спектралните характеристики на структурите с Al и Ni контакти показват максимум на спектрална чувствителност в интервал 280÷330 nm. Волт-амперните характеристики са измерени в интервал 4÷30 V на тъмно и при осветяване със син LED (380 nm) и Hg лампа 50 W (365 nm). При осветяване с Hg лампа и прилагане на 6÷10 V напрежение, фототокът нараства на порядък, което показва, че структурите с Al и Ni контакти са подходящи за UV сензори.