Photoelectrical Characteristics of TiO_2-Si Heterostructures

V.M. Kalygina, I. S. Egorova, I.A. Prudaev, O. P. Tolbanov
Functional Electronics Laboratory
Tomsk State University, TSU
Tomsk, Russia
Kalygina@ngs.ru

***Abstract*—The influence of thermal annealing on photoelectrical properties of TiO_2-n-Si structures is studied. It is shown that growth of reverse current during radiation begins at threshold voltage U_t. Its value depends on annealing temperature. Persistent photoconductivity is observed only in such TiO_2-Si structures if the oxide titanium film contains anatase crystallites. Photoconductivity is observed in such TiO_2-Si structuresif the oxide titanium film contains anatase crystallites.**

Keywords—titanium oxide films, thermal annealing, current-voltage characteristics, photocurrent, persistent photoconduction, charge carrier generation

I. Introduction

Among various metal oxides titanium oxide has a special place due to a number of unique properties such as high transparency in the visible range, photocatalytic activity, a large band gap, high dielectric permittivity. The relative ease of production and the possibility of varying its properties by external influences (redox, treatment in different atmospheres, doping impurities, radiation exposure, etc.) made this material attractive for practical application. It is proposed to use of titanium oxide films in light-emitting devices, memristors, in spintronic devices, photovoltaic cells and so on. To achieve the desired quality of the coatings after deposition annealing process in which the film structure changes from amorphous to crystalline phase are often used. As a result surface roughness, the microhardness and the dielectric constant change.

This paper presents the results of studies of the effects of radiation with λ = 400 nm on the forward and reverse currents of TiO_2-n-Si structures before and after annealing in argon at 500 and 750ºC.

II. Experimental Procedure

Titanium oxide film with thickness of 70 nm were prepared by magnetron sputtering on silicon epitaxial layer with a donor concentration $N_d = 7{\cdot}10^{14}$ cm^{-3}. TiO_2 target was used. Before deposition of dielectric film the silicon wafer was exposed to the chemical cleaning which included the followings processes:

1 depriving of fat an izopropil alcohol;

2 boiling in a toluene (two times for five minutes);

3 boiling in a 50% solution of sulphuric acid (H_2SO_4 : H_2O = 1:1) (two minutes);

4 cooling of silicic substrate in an aquatic bath-house to the temperature of 30-40°C;

5 washing in running deionizovannoy water (5 minutes);

6 drying of substrate in an acetone.

After sputtering the titanium oxide film a Si-substrate with dielectric film was separated into several parts. One part was not subjected to annealing, and the two parts were annealed in an argon atmosphere for 30 minutes at temperatures T_a = 500°C or 750ºC.

For the measurement of electrical characteristics on the surface of TiO_2 and a opposite side of a silicon wafer V/Ni electrodes were deposited by electron beam evaporation: to silicon – a continuous electrode and on the titanium oxide surface the electrodes were sputtered through masks. The diameter of the electrode to the TiO_2 (gate) was 1.15 mm, the area $S = 1.04{\cdot}10^{-2}$ cm^2.

The current-voltage characteristics (CVC) were measured with automatic system capable of measuring currents in the range of 10^{-10} – 10^{-2} A. The voltage was measured in range of ± 30 V.

The photoelectric characteristics were studied with LED (λ = 400 nm). The structures were lighted up from the side of titanium oxide film. The values of optical power P varied by changing the LED current. For some samples measuring current-voltage characteristics (dark and light) were carried out using a measuring complex based on Keithley 2636A and laser diode Nichia NDV4642VFR (λ = 405 nm).

III. Results of Experiment

Fig. 1 shows the effect of radiation with λ = 400 (405) nm on the TiO_2-n-Si structure without annealing when positive potentials are on the gate. The currents at positive potentials on the gate increase during exposure to radiation, starting with the low voltages (Fig. 1) unlike photodiodes with Schottky barrier and metal-SiO_2-n-Si structures. The curve, marked D, corresponds the original dark forward current, measured before illumination of the sample with λ = 400 nm. The curve

This work was supported by The Ministry of Education and Science of the Russian Federation (Project No 3.1206.2014)

L shows current during radiation and curve D1 corresponds the current after turning off the light.

Currents at negative potentials at the gate show significantly greater sensitivity to light (Fig. 2). For the structure without anneal increasing of reverse current under the influence of radiation is observed at voltages U_t greater than 2 V

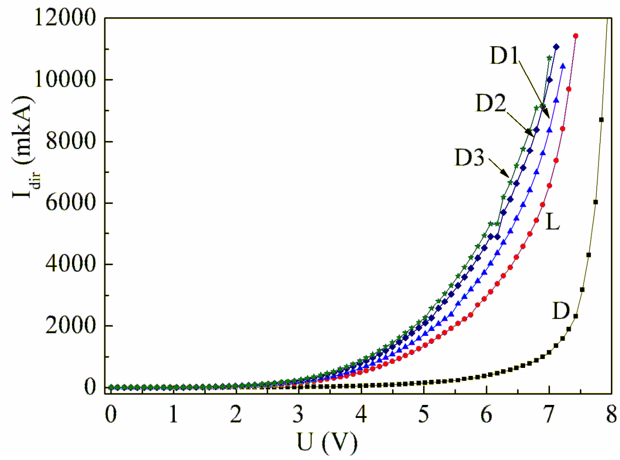


Fig. 1. Currents at positive potentials of the gate without and during exposition to radiation with λ = 400nm

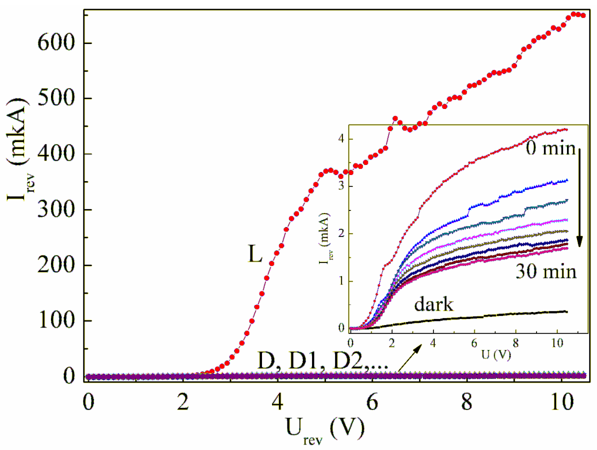


Fig. 2. Currents at negative the potentials of the gate without and when exposed to radiation with λ = 400nm. The insert shows reveres currents after turn off the light in more detailed scale

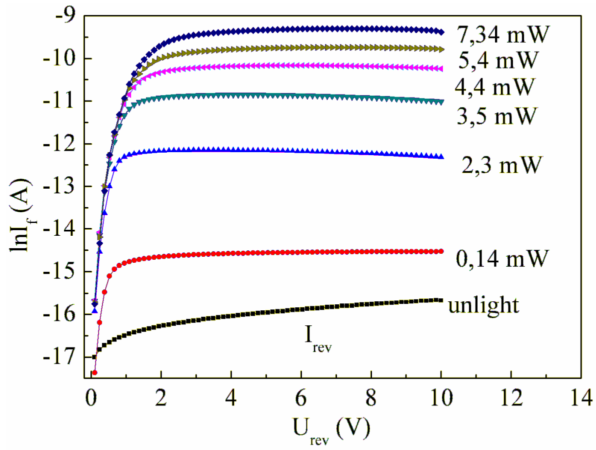
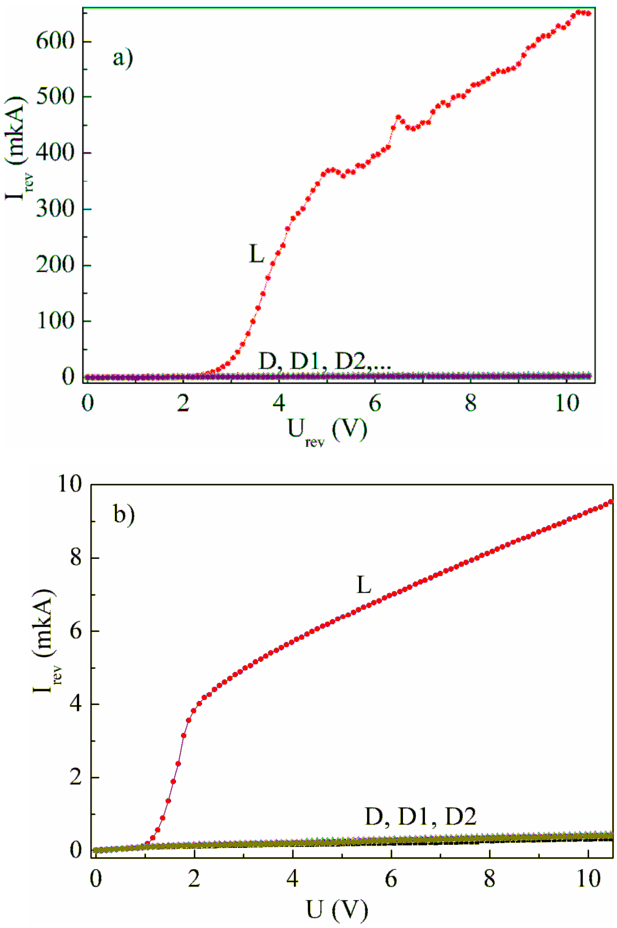


Fig. 3. Dependence of the photocurrent for the structure without annealing; λ = 400 nm; P = 0,14; 2,3; 3.5; 4.4; 5.4; 7.34 mW

With the increase of voltage the photocurrent I_f increases and tends to saturate at the bias voltage greater than 2 V (Fig. 3). The lower curve on Fig. 3 shows a reverse current before illumination for comparison. The increase in optical power leads to an increase I_f linearly.

For structures annealed at 500°C the increasing of reverse current during light exposition is observed at voltage U_t which in two times less than that of structures without annealing (Table, Fig. 4b).



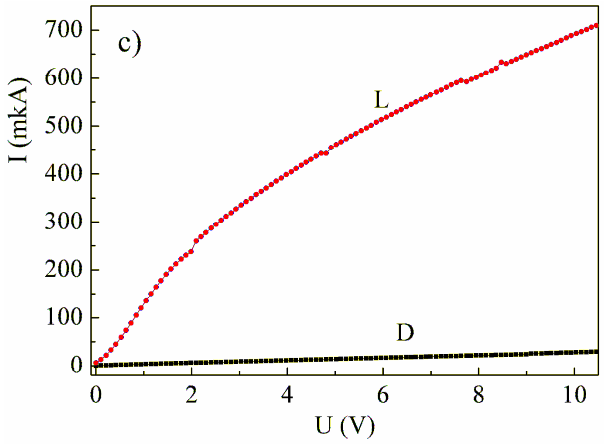


Fig. 4. Currents at negative potentials of the gate; annealing temperature: $0^{O}C$ (a), $500^{O}C$ (b), $750^{O}C$ (c).

Dark reverse currents of sample annealed at $500^{O}C$ and photocurrent are less than the current of the structures without annealing almost two orders (Table).

TABLE I. THRESHOLD VOLTAGE OF REVERSE CURRENT INCREASE AT TURN ON RADIATION; PHOTOCURRENT VALUE AT U = 10 V; BAND GAP OF TIO_2 FILM DEPENDING ON ANNEALING MODE

processing mode	**threshold voltage U_t, V**	**photocurrent at maximum voltage (U=10 V), µA**	**E_g, eV**
without annealing	2.2	600	3.0
annealing at $500^{O}C$	1.1	8	3.2
annealing at $750^{O}C$	0	700	3.0

A characteristic feature of reverse currents changing after switching off the light is the appearance of residual currents. The curves, marked D1, D2, D3 and etc correspond to currents which are not equal to the values I_d before illumination (not evidently at Fig. 4b).

However, in one month dark currents of the samples annealed at 500°C become in 2 times lower in comparison with the initial values of currents I_d. This effect can be used for practical purposes as a method for reducing of leakage currents in MIS structures with titanium oxide film as dielectric.

Fig. 5 shows the dark currents at negative potentials of the gate depending on the time after the light is turned off. Numbers near curves correspond to the temporal intervals after the shutdown of light

The curve for the dark current immediately after switching off the lighting is significantly higher than the initial one (D). This phenomenon is called frozen photoconductivity (persistent photoconductivity).

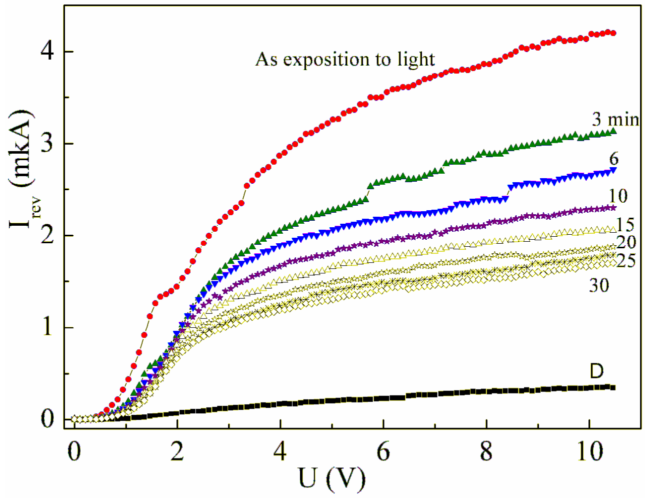


Fig. 5. FDark reverse currents of sample annealed at $500^{O}C$ depending on the time after the light is turned off

At a fixed bias voltage the value of the current decreases exponentially and is described by the formula:

$$y = A_1 \cdot e^{(\frac{-x}{t_1})} + A_1 \cdot e^{(\frac{-x}{t_2})} + y_o \quad (1)$$

where $A_1 = 1.11$, $A_2 = 1.32$, $t_1 = 2.60$, $t_2 = 21.58$, $y_0 = 1.08$

In contrast to the above results samples annealed at 750°C show increase of reverse current during light exposition beginning at $U_t = 0$ V and persistent photoconductivity is absent (Fig. 4c). At positive and negative potentials at the gate direct and reverse currents returned to baseline values without inertia after turning off the lights. Besides it, photocurrent values are almost such magnitude as that of the samples without anneal (Table). Thus persistent photoconductivity is observed in such TiO_2-n-Si structure if the titanium oxide film contains anatase crystallites. For these hetero structures there is threshold voltage U_t beginning from which reveres current increases when the sample is exposed to light.

IV. Discussion of Experimental Results

To discuss the results of the experiment we was used the energy diagram shown on Fig. 6. The values E_g of the band gap and electron affinity of the materials included in the structure were taken into account. It should be taken notice to a small value of the conduction band discontinuity ($\Delta E_c = 0.3$ eV) and large valence band discontinuity ($\Delta E_v = 2.3$ eV) as well as small bending bands on the silicon surface, which does not exceed 0.2 eV.

At the positive potentials on the gate, electrons are injected from the silicon into titanium oxide. Even at small bias voltage barrier at the TiO_2-n-Si interface disappears and all voltage applied to the structure drops in the dielectric. C

urrent through the sample is determined by processes in the film TiO_2. Direct current-voltage characteristics are determined by space charge limited currents (SCLCs) in a dielectric with traps exponentially distributed on energy [2].

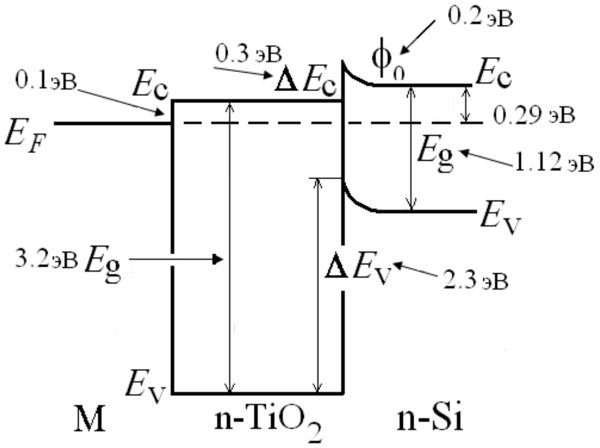


Fig. 6. Energy diagram of TiO_2-n-Si hetero structure

A distinctive feature of these structures is the presence of photo resistor effect at positive potentials on the gate (Fig. 1). When the sample is exposed to radiation currents increase for all bias voltages, begining from a minimum, and return to baseline values after turn off light only after some time. The photoconductive effect is explained with an extremely small width of SCR in silicon at positive potentials at the gate. As a results Si wafer is photo resistor during exposition.

At negative potentials on the gate the electrons from metal gate are injected in the TiO_2, while the space charge region (SCR) is formed in Silicon. The voltage drop is distributed between titanium oxide film and SCR in silicon [2].

The appearance of the photocurrent in the samples TiO_2-Si is due to the generation of electron-hole pairs in the titanium oxide film and silicon. The peculiarity of the influence of radiation with λ = 400 nm is the presence of the threshold voltage corresponding to increase of the photocurrent in the samples without annealing and annealed at 500°C during exposition.

The threshold voltage is related to the low transparency of TiO_2 films at λ= 400 nm [3]. A photocurrent in the structures exposed to annealing at 500°C is almost on two orders less as compared to that for structures without annealing and with annealing at 750C (Table).

After annealing at 500C anatase crystallites prevail in TiO_2 film. Anatase bandgap E_g = 3.2 eV exceeds the quantum of energy of falling light. In this case probability of appearance of excess electrons and holes due to their transition from the valence band of TiO_2 in conduction band is improbable. It is supposed that in this case photocurrent is conditioned by a generation of charge carriers only in silicon SCR.

Higher values of photocurrents in structures without annealing and after annealing at 750°C are explained to a noticeable contribution of generation processes in the oxide of titan in the amorphous state and in the phase of rutile with the bandgap of E_g = 3.0 eV.

From comparison of values of photocurrents (Table) it is possible to suppose that generation processes in titanium oxide film, but not in SCR of silicon give basic contribution to I_f of studied structures.

It is assumed that the persistent photoconductivity in the structures of TiO_2-n-Si is explained a large potential barrier (2.3 eV) on the interface of TiO_2-n-Si (Fig. 6) which hinders the transition of holes, generated during of radiation, from the valency band of silicon in valency band of titanium oxide.

V. Conclusion

Influence of the thermal annealing on photo-electric characteristics of TiO_2–n-Si structures with the film of titanium oxide, got HF magnetron sputtering is studied. At positive potentials and during radiation with λ = 400 nm currents increase through structures. Thus photo resistance effect is observed.

In structures without annealing and after annealing at 500°C there is the threshold voltage of growth of reverse-current at the action of light with λ = 400 nm. The effect of the persistent photoconductivity is observed in structures with film of titanium oxide, containing the crystallites of anatase. Enhanceable values of reverse current which presents in structures after the shutdown of light are explained a large potential barrier to the transition of holes from Si in TiO_2.

References

[1] V.M. Kalygina, V.A. Novikov, Y.S. Petrova, O.P. Tolbanov, E.V. Chernikov, S.Y. Tsupy, T.M. Yaskevich. “Influence of thermal annealing and exposure to oxygen plasma structures on the properties of TiO2-Si”, Semiconductor Physics and Technology, 2014, .v. 48, №. 7, pp. 989-994

[2] V.M. Kalygina, I. S. Egorova, I.A. Prudaev, O.P. Tolbanov, Photoelectrical characteristics of TiO2-Si hetero structures (in press).

[3] Yu.V Gerasimenko, V. Logacheva, A.M. Khoviv, Sintez and properties of thin-ilms of titania, the Condensed environments and mezhfaznye scopes, 2010, v. 12, № 2, pp. 113—118.