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Conduction mechanism of metal-TiO_2-Si structures

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***Abstract*— The influence of annealing of titanium oxide films on the currents of metal-TiO_2-n-Si structures was investigated. It has been shown that regardless of the annealing temperature the conductivity of structures at positive potentials on the gate is determined by currents limited by the space charge in the dielectric with traps exponentially distributed on energy. At negative potentials the main contribution to the current is the thermal generation of charge carriers in the space charge region in the silicon. Interface properties of TiO_2-n-Si depend on the structural and phase state of the titanium oxide film which are determined by the annealing temperature.**

Keywords—titanium oxide films, annealing temperature, current-voltage characteristics, space charge limited current, charge carrier generation

I. INTRODUCTION

Titanium oxide films can be the key elements in different electronic devices such as memristors, photovoltaic cells, transparent electrodes, gas sensors, etc. Breakthrough in development of silicon microelectronic is associated with an increased informative capacity that can be achieved by replacing traditional SiO_2 on dielectrics with high dielectric permitivity ε. One of the possible candidates for the role of alternative dielectric in MOS-IC is a titanium oxide with a band gap E_g = (3.0 – 3.2) eV and ε = 30 -80 depending on the structure and phase composition.

To improve the efficiency of TiO_2 application in devices for different purposes it is necessary a deep understanding of the physical processes occurring in the oxide films depending on the method of fabrication, the subsequent technological treatments and design features of the devices. In this report we present the results of a study of metal-TiO_2-Si structures in order to clarify the mechanism of conductivity.

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}. The target was TiO_2. Detailed preparation of samples is described in [1].

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

The structure and phase composition of TiO_2 films were determined by X-ray diffraction analysis using a Shimadzu XRD-Position 6000 (anode: Cu (CuKα 1.54056Å).

For the measurement of electrical characteristics on the surface of TiO_2 and the opposite side of a silicon wafer V/Ni electrodes were deposited by electron beam evaporation: to silicon – a continuous electrode and on the surface of the titanium oxide 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.

To measure the current-voltage characteristics (CVC) the automatic system was used in the current and voltage ranges of 10^{-10} – 10^{-2} A and ± 30 V, respectively. For some samples measurements of current-voltage characteristics were carried out using Keithley 2636A. In the study of the temperature dependence of the electrical characteristics a thermostat was used with the temperature precision of 0.1^{O}C .

III. RESULTS OF EXPERIMENT

As deposited titanium oxide films are amorphous. According to X-ray diffraction (XRD) spectra of samples annealed at 500°C on the background of the amorphous phase, there are small reflections at 2θ = 25.2, 27.4 and 56.7 degrees, which belong to crystallites of anatase with orientation (101) and rutile planes (110) and (220) respectively (Fig. 1). Thus, after annealing at 500°C in an argon the structure of titanium oxide films becomes amorphous-crystalline, i.e. in the amorphous matrix individual crystallites of anatase and rutile appears.

After annealing at 750ºC amorphous phase disappears, the film becomes polycrystalline. The phase of anatase disappears completely and only rutile crystallites present with the (220) - reflex when 2θ = 56.7 degrees (Fig. 2). The inset in Figure 2 in a more detailed scale shows reflexes, indicating the presence in the oxide film of the crystallites of rutile (110) – 2θ = 27.4 deg. and (210) – 2θ = 44.1 deg. Thus, by raising the annealing temperature mobility of the oxygen atoms increased, and at the same concentration of O_2 amorphous-crystalline film transformed into a polycrystalline state.

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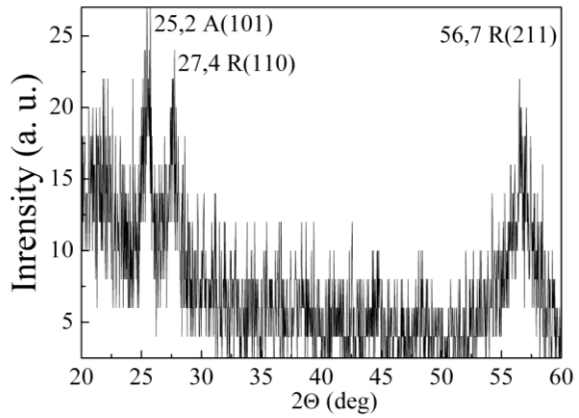

Fig. 1. X-ray diffraction spectra of the titanium oxide film after annealing in argon at 500ºC

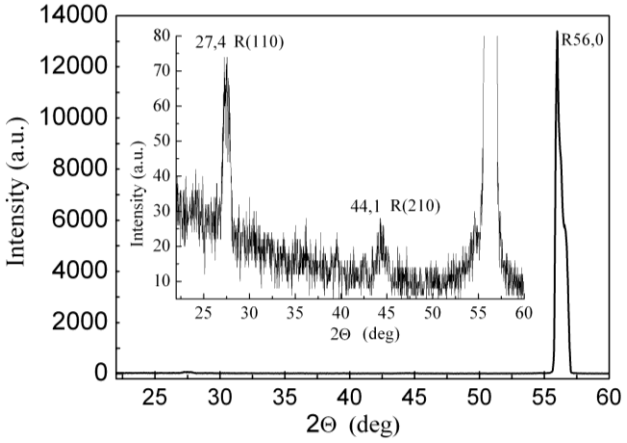

Fig. 2. X-ray diffraction spectra of the titanium oxide film after annealing in argon at 750ºC

At negative potentials at the gate in the double logarithmic scale dependence of the reverse current (I_{rev}) on voltage is represented by a straight line with a slope m = 0.5 in the voltage range $1 \cdot 10^{-3}$ – 10 V. With increasing temperature, the reverse current increases exponentially (Fig. 5).

Positive potentials on the electrode to TiO_2 corresponde to direct current-voltage characteristics (CVC), the reverse current-voltage characteristics are observed at negative potentials. There are three sections on the direct current-voltage characteristic in double logarithmic scale regardless of the annealing temperature, each of which is determined by the degree of dependence of current on voltage as $I \sim U^m$ (Fig. 3). The first section is observed at bias voltages up to 0.1 V with $m \approx 1$. In the second section ($0.1 \le U \le 1.0$ V) the value of m depends on the annealing temperature and lies in the range 2.8 – 4.9 (Table) and reduced to 2 at voltages up above 0.9 V (third section).

In the voltage range corresponding to the second section of the CVC, direct current (I_{dir}) depends weakly on temperature. On Fig. 4 it is shown the temperature dependence I_{dir} of the sample without annealing. Similar data were obtained for the structures after annealing at T_a = 500 and 750°C. It should be noted that when T_a is increased the voltage increases at which current exhibits a weak dependence on temperature.

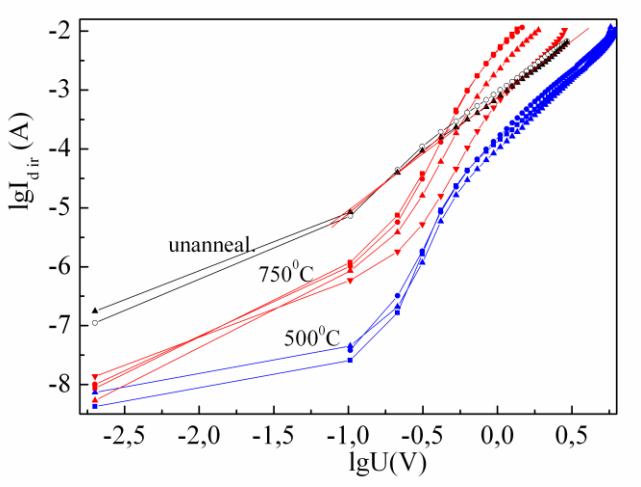

Fig. 3. Direct currents of the samples without and after annealing

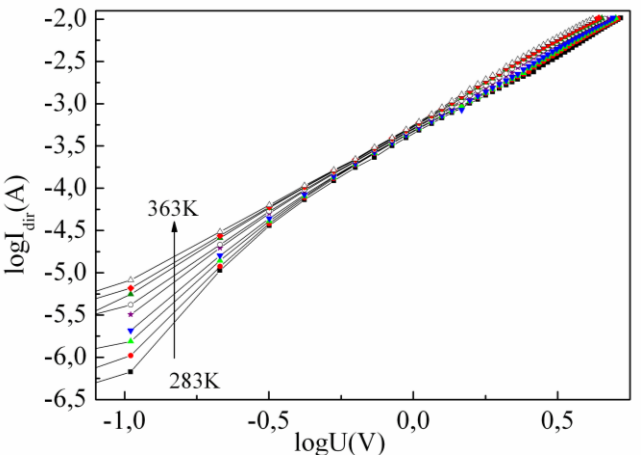

Fig. 4. The temperature dependence of the forward current of the sample without annealing

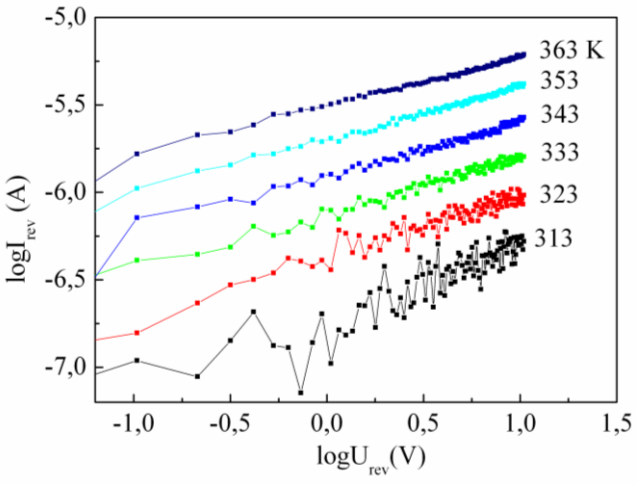

Fig. 5. The temperature dependence of the reverse current of the sample without annealing

TABLE I. THE VALUES OF TG THE SLOPE OF THE CVC IN THE SECOND PORTION, THE DIELECTRIC CONSTANT OF THE TITANIUM OXIDE FILM, THE ENERGY POSITION OF THE RECOMBINATION LEVEL

Annealing regime	**m for II section**	**ε**	**ΔE_{ts}, эВ**
without annealing	2.8	32	0.44+/-0.07
annealing at 500°C	4,9	46	0,52+/-0,04
annealing at 750°C	4,6	44	0,81+/-0,01

IV. DISCUSSION OF EXPERIMENTAL RESULTS

To discuss the results of the experiment we use the energy diagram shown in Fig. 6, taking into account the values of the bandgap E_g and electron affinity of the materials of the structure. Attention should be paid to a small value of the conduction band discontinuity (ΔE_c = 0.3 eV) and large valence band discontinuity (ΔE_v = 2.3 eV) as well as small band bending 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 voltages the barrier at the TiO_2-n-Si interface disappears and all voltage applied to the structure drops in the dielectric. Current through the sample is determined by processes in the TiO_2 film.

From the analysis of current-voltage characteristics represented in the double logarithmic scale, it follows that the conductivity of TiO_2 films is determined by the space charge limited current (SCLC) in a dielectric with traps exponentially distributed by energy. The dependence of the current density on voltage is described by the expression [2]

$$J = N_c \mu e^{1-l}\left[\frac{\varepsilon\varepsilon_0 l}{N_t(l+1)}\right]^l \left(\frac{2l+1}{l+1}\right)^{l+1}\frac{U^{l+1}}{L^{2l+1}} \qquad (1)$$

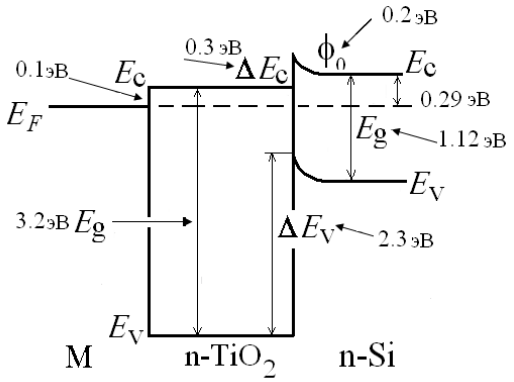

Fig. 6. Energy diagram of TiO_2-n-Si structure

where N_c – effective density of quantum states in the conduction band of titanium oxide; ε –dielectric permittivity; ε_0 – electric constant; μ – electron mobility; N_t – trap concentration in the TiO_2 film; e – electron charge. According to equation (1) from the slope of the CVC in double logarithmic scale the exponential power l = m – 1 can be defined. The weak temperature dependence of the currents (Fig. 4) is consistent with the assumption of SCLC in the samples.

Voltage transition from Ohm's law for SCLC is described by [2]

$$U_{\Omega\to T} = \frac{eL^2}{\varepsilon\varepsilon_0}\left(\frac{l+1}{2l+1}\right)^{(1+l)/l} \times N_t\left(\frac{n_0'}{N_c}\right)^{1/l}\left(\frac{l+1}{l}\right) \qquad (2)$$

where N_t – the concentration of traps in the dielectric. Using the experimental data and (2) it was found that $N_t = 5\cdot10^{17}$ and $1\cdot10^{17}$ cm $^{-3}$ for structures without annealing and after annealing at 750°C, respectively. When calculating N_t concentration the n_0' was assumed to be 10^{17} cm^{-3}, $N_c = 2\cdot10^{18}$ cm^{-3} [3]. Ten-fold increase of n_0' leads to two-fold increase of N_t

The assumption about the main role of the insulator in processes in the TiO_2-n-Si structures at positive potentials on the gate is confirmed by measurements of the current-voltage characteristics.

Fig 7 shows the C–U characteristics of the investigated samples measured at a frequency of 1 MHz. Horizontal line marked capacitance values C_{fb} corresponding to the flat-band voltage (U_{fb}). Flat-band voltage was found using the experimental curves C(U) (Fig. 6a) and calculated values C_{fb} in the flat-band mode [4].

$$C_{fb} = \varepsilon_s\varepsilon_0 S/[L + (\varepsilon/\varepsilon_s)L_n] \qquad (3)$$

$$L_n = [kT\varepsilon_s\varepsilon_0/(e^2 n_0)]^{1/2} \qquad (4)$$

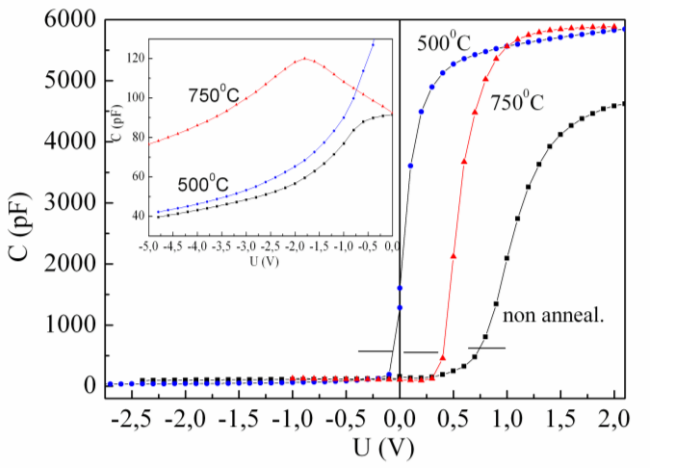

Fig. 7. Capacitance-Voltage characteristics of the metal TiO_2-n-Si structures. The insets in a more detailed scale shows CU dependence at negative potentials at the gate

where ε_s – the dielectric permittivity of silicon; n_0 - equilibrium concentration of electrons in silicon; k - Boltzmann constant; T – the absolute temperature. According to Fig 6a irrespective of the annealing temperature at voltages less than one volt TiO_2-n-Si structures are in the flat band mode. With further increase of the voltage the band bending at the Si surface becomes positive and the structure enters the enrichment mode.

From Fig. 1 it is seen that maximum currents observed in structures without annealing, and the minimal currents observed in the samples after annealing at 500°C. This behavior of the currents is related to structural phase transformations in titanium oxide film after annealing. Smaller currents after annealing of TiO_2 films at 500°C are associated with a greater band gap of anatase compared with rutile and amorphous titanium oxide. The insets in a more detailed scale show CU and GU dependences at negative potentials at the gate.

At negative potentials of the gate the space charge region (SCR) is formed in the silicon and the voltage drop is distributed between the TiO_2 film and SCR in silicon. Current through the structure I_{rev} is due to the generation of electron-hole pairs in the SCR silicon and is described by the expression [5].

$$I_{rev} \approx I_g = \frac{S\, e\, n_i\, d(U_{scr})}{2\tau_i} \qquad (5)$$

where n_i и τ_i – concentration and life time of charge carriers in intrinsic semiconductor; $d(U_{scr})$ – the width of the space charge region. In (5)

$$U_{scr} = U - I_g R_d \qquad (6)$$

where R_d – resistance of the TiO_2 film. Current dependence on the voltage is given by

$$I_g = A\sqrt{\varphi_s + (U - I_g R_d)}\,, \qquad (7)$$

where φ_s – surface potential on TiO_2-Si interface,

$$A = \frac{S\, e\, n_i}{2\tau_i}\sqrt{\frac{2\varepsilon_s\varepsilon_0}{eN_d}}\,. \qquad (8)$$

Solving the equation (7) with respect to I_g, we find that

$$I_g = \frac{A^2 R_d}{2}\left[\sqrt{1 + \frac{4(\varphi_s + U)}{A^2 R_d^2}} - 1\right]. \qquad (9)$$

Numerical analysis shows that in (9) $AR_d << 1$ and

$$I_{rev} = I_g \approx A(\varphi_s + U)^{1/2}\,. \qquad (10)$$

At $U >> \varphi_s = 0.2$ V a reverse current-voltage characteristics in a double-logarithmic scale are represented as a line with a slope equal to 0.5, which corresponds to the data in Fig.5.

Temperature dependence of the reverse current is determined by

$$A = \sqrt{\frac{2\varepsilon_s\varepsilon_0}{eN_d}}\cdot\frac{S\,e}{\tau_{p0}}N_v(T^{3/2})\exp\left[-\frac{(E_g - \Delta E_t)}{kT}\right], \qquad (11)$$

where E_g and N_v – the band gap and the effective density of quantum states in the valence band of silicon, respectively; $\Delta E_t = E_c - E_t$ – the energy position of the recombination level E_t relative to the bottom of the conduction band E_c in silicon; τ_{p0} – hole lifetime, when all the recombination levels are occupied by electrons. According to equations (10) and (11) the reverse current at voltages significantly greater than φ_s, should increase with temperature exponentially with an activation energy which equals $(E_g - \Delta E_t)/k$. Using the experimental temperature dependence of the structure reverse current without and after annealing, values ΔE_t was found which are listed in the Table.

One possible explanation for the differences in the values of ΔE_t, may be the assumption that most part of the electron-hole pairs that have emerged due to heat generation recombines via surface states at the TiO_2-Si (E_{ts}). Properties of the TiO_2-Si interface are determined by the structure and phase composition of the oxide film. ΔE_{ts} values for amorphous and amorphous-crystalline TiO_2 films coincide with the error in the determination (Table).

For polycrystalline TiO_2 film (rutile) E_{ts} recombination level is in the lower half of the band gap, which implies substantial changing of the TiO_2-Si interface. Capacitance-voltage and conductance-voltage characteristics at negative potentials at the gate, confirm the significant changes on the interface of TiO_2 -Si in the transition from amorphous to polycrystalline state (Fig. 7, 8 inset).

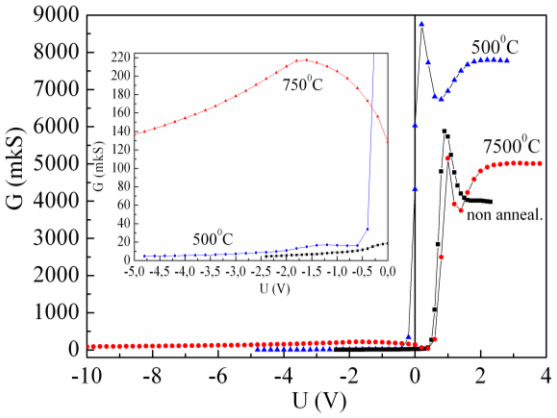

Fig. 8. Conductance-voltage characteristics of the metal TiO_2-n-Si structure. The insets in a more detailed scale shows GU dependence at negative potentials at the gate

After annealing at 750°C on CU curves at negative voltages, there is a maximum, indicating the emergence of a new group of surface states (E_{ts}) is not typical for the structures without annealing and after annealing at 500°C.

After annealing at 750°C on CU curves at negative voltages, there is a maximum, indicating the emergence of a new group of surface states (E_{ts}) is not typical for the structures without annealing and after annealing at 500°C. A similar peak is present at negative potentials at GU dependencies. In contrast to other samples GU dependencies of structures annealed at 750°C, describes a curve with two maxima: one at U = 1,0 V, while the second at U = – 1.7 V (Fig. 8). Special behavior of C–U and G–U characteristics of TiO_2-Si structures after annealing at 750°C are explained with an increase in the differences between crystal lattice parameters of polycrystalline oxide film and silicon.

V. Conclusion

The influence of annealing temperature in argon on the currents of metal-TiO_2-Si structures at a constant signal at positive and negative potentials at the gate was investigated. The results lead to the following conclusions:

1. Regardless of the annealing temperature the conductivity of the structures at positive potentials on the gate is determined by space charge limited current in the dielectric with traps exponentially distributed by energy in a band gap.

2. At negative potentials, the main contribution to the current gives the thermal generation of electron-hole pairs in the space charge region in the silicon.

3. Properties interface TiO_2-Si depend on the structural state of the phase of the titanium oxide film, which are determined by the annealing temperature.

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