Photoelectrical properties of TiO$_2$-Si structures

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Abstract. The effect of thermal annealing at 500 and 750ºC as well as treatment in oxygen plasma on electrical and photoelectrical characteristics of TiO$_2$-Si structures were investigated. TiO$_2$ films were deposited on n-Si substrates by magnetron sputtering. It was found that in the structures annealed at 500ºC and treated in oxygen plasma a substantial part of the enhanced photocurrent was observed over a long time after removing of illumination with $\lambda = 400$ nm.

1. Introduction
Anatase and rutile are two stable crystalline phases of TiO$_2$ that have a vast variety of applications. Titanium oxides are chemically stable, relatively hard and transparent. Its particularities are high dielectric constant and photocatalytic activity. Due to high refractive index TiO$_2$ is interesting for optical applications, e.g. antireflection coatings, narrow band filters, and optical waveguides. TiO$_2$ phases are wide gap semiconductors with a large range of electrical properties depending on chemical composition. In this paper the results of effects of thermal annealing and oxygen plasma treatment on electrical and photoelectrical characteristics of TiO$_2$-n-Si structures are presented.

2. Experiment details
TiO$_2$ films with thickness 90 – 100 nm were fabricated by magnetron depositing on n-Si substrates. TiO$_2$ was used as a target. TiO$_2$-n-Si structures were annealed in argon at 500 or 750ºC. Some part of the samples were treated with oxygen plasma during 20 min at 50ºC before annealing. Structural characteristics of the samples were measured by X-ray diffraction and atomic force microscopy (AFM), Metal Ni/V contacts were deposited on TiO$_2$ and Si substrate. For investigation of photoelectrical characteristics LED with $\lambda = 400$nm was used. Light power $P$ was changed in 20 – 520mkW interval.

3. Results and discussion
As-deposited TiO$_2$ films had amorphous structure. Figure 1 indicates the results for films after annealing at 500ºC. XRD spectra contain amorphous matrix peaks at $2 \Theta = 25.2^\circ$, $27.4^\circ$ and $56.7^\circ$ which belong to anatase (101) crystalline as well as rutile (110) and (211) crystalline respectively. If before annealing TiO$_2$ films had been treated in oxygen plasma at 50ºC the XRD patterns show two new peaks: at $2 \Theta = 38^\circ$ which corresponds to anatase crystalline (211) and $2 \Theta = 44.1^\circ$ corresponds to rutile crystalline (210) (Figure 1b). Besides, effect of oxygen plasma leads to increasing of antecedent peaks about two times in XRD spectra of TiO$_2$ films.
After annealing at 750°C amorphous phase vanishes and the film becomes polycrystalline (Figure 2a). Anatase phase disappears and in TiO₂ film only rutile crystalline remain mainly with crystal orientation (220) – peak at 2Θ = 56.7 degree. Insert in figure 2a shows detailed XRD pattern of TiO₂ film and it can be seen the peaks at 2Θ = 27.4 and 44.5 degree which belongs rutile crystalline. Preliminary expose of TiO₂ films to oxygen plasma before annealing at 750°C does not change their structure (Figure 2b).

Figure 1. XRD patterns of TiO₂ film after annealing in argon at 500°C: a – without treatment in oxygen plasma; b – with treatment in oxygen plasma before annealing

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Figure 2. XRD patterns of TiO₂ film after annealing in argon at 750°C: a – without treatment in oxygen plasma; b – with treatment in oxygen plasma before annealing

According to AFM images the roughness of TiO₂ films is 8 – 10 nm after annealing at 500°C (Figure 3a, 3b). The morphology of films significantly varied as result of their treatment in oxygen plasma. The influence of oxygen on TiO₂ films results in merging of irregularities and formation of some grain-like structure (Figure 3c, 3d). The size of grains increases at substrate plane after influence of oxygen plasma and it is about 100 nm.

It is evident from figure 4a and 4b that grain size increases with rise of annealing temperature. As a rule annealing of TiO₂ films at 750°C results in increasing of grains perpendicularly to substrate. The effect of growth temperature is also reflected in the case of root-mean-square surface roughness and their values increases to 20 nm (Figure 4b). In addition new crystalline particles nucleate with size of grains equal 20 – 50 nm (Figure 4a).
After oxygen exposure on TiO$_2$ films and subsequent annealing in argon at 750°C it can be seen intergrowth of crystalline and formation of large particulars with size 150-200 nm (Figure 4c). The surface roughness decreases to 10 nm.

Figure 3. AFM images of TiO$_2$ films formed on Si substrates: a, b – after annealing at 500°C; c, d – treatment in oxygen plasma before annealing at 500°C

The TiO$_2$-n-Si structures showed rectifying properties. At positive potentials on the gate direct current-voltage (I-U) characteristics changed very slightly even under illumination with light power $P = 520$ mkW. Under illumination at negative potential on a gate the photocurrent appeared. Its value depended on optical power, voltage (U) at structure and treatment regime (Figure 5). Enhancement of photocurrent with increasing voltage was observed at $U \geq 2$V for samples annealed at 500°C.

An important feature of structures behavior is continuous photocurrent decay after switch of light (Figure 6). Decrease of photocurrent as a function of time is described by exponential law. Time constant does not depend on voltage at $U \geq 2$V and equals 22 ± 2 min at room temperature. Persistent photocurrent is absent in structures annealed at 750°C. After illumination with light power 520 mkW dark reverse current of the structures annealed at 750°C in argon without a treatment in oxygen plasma decreased and its value was about two times less than initial dark current. This effect did not monitored in structures treated in oxygen plasma before annealing at 750°C. Experimental data are explained under consideration of phase and structural changing in TiO$_2$ films and the interface Si-TiO$_2$. 


Figure 4. AFM images of TiO$_2$ films formed on Si substrates: a, b – after annealing at 750°C; c, d – treatment in oxygen plasma before annealing at 750°C.

Figure 5. Dependence of photocurrent on voltage: a – without treatment in oxygen plasma, annealing at 500°C; b – with treatment in oxygen plasma before annealing at 500°C.
Photocurrent is absent in $0 \leq U \leq 1$ V interval. It is explained by forming of depletion regime and appearance of inversion layer. At very low frequency (continuous current) all bias voltage is applied on TiO$_2$ and photocurrent is defined by band to band generation of electron-hole pairs in dielectric film.

![Figure 6. Change of dark reverse I-U characteristics of the structure (20min, 500 °C) after switch off light with $P = 520$ mkW at different time intervals; $I_L$ is current at $P = 520$ mkW; $I_d$ - initial dark current.](image)

4. Conclusion
The influence of thermal annealing and treatment in oxygen plasma on electrical and photoelectrical characteristics of TiO$_2$-Si structures have been investigated. It has been shown connection of structure and phase composition of TiO$_2$ films with photoelectrical characteristics of TiO$_2$-Si structures. Slow decreasing of reverse current after switch off light is explained by persistent photoconductivity which takes place in TiO$_2$ – n-Si structures only after define technological processing.