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Modification of Phase Boundaries and Oxide Layer of Ti – TiO_2 – Oxidant System, by Intensive Thermo – Chemical Oxidation with Rapid Thickness Growth of Dielectric Oxide Layer n–Conductivity Type

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Abstract: Titanium oxidation process is thermodynamically spontaneous, its speed depends on kinetic and diffusion process parameters. According to optical measurements results, the oxide layer formed on titanium has a thickness of only 1.7 nm. A layer of this thickness is formed at room temperature within two hours, and in 40-50 days it grows to 3.5 nm. Created under natural conditions, TiO_2 is a non-stoichiometric dielectric oxide of n-type conductivity.

The goal of this work is to significantly speed up the oxidation process by thermo-chemical oxidation and achieve oxide thicknesses over 100μm. An intensive thermo-chemical process creates disorders with oxygen vacancies excess ($O_{\square}^{\bullet\bullet}$) and with a smaller representation of interstitial disorders ($\mathrm{Ti}_{\bullet}^{\bullet}$).

In this work, starting from the mentioned disorders - defects, by thermo-chemical oxidation of Ti - TiO_2 - oxidant system, by choosing numerous oxidants, a composite system was obtained with a significant increase in disorder degree of active centers - defects about 10^{18} to $10^{20}/cm^3$. Thus, the significantly disordered structure of Ti – TiO_2 – oxidant system can be a very active dielectric diode in Ti – TiO_2 – M system (where M is some vaporized metal). Such a diode has stable rectification properties at high temperatures up to 10^6 times, which makes it more reliable compared to the active element of semiconductive p-n diode system.

Keywords: Ti – TiO_2 – oxidant system, Non-stoichiometric dielectric oxide, Thermo-chemical oxidation, Positive space charge, Dielectric diode rectifying properties.

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1 Introduction

1.1 Introduction to subject processes

Bearing in mind that results analysis and discussion of the TiO_2 disorder model are related to non-stoichiometry and numerous defects, symbols and possible interactions of defects in Ti - TiO_2 - oxidant system are presented. This type of symbolism was introduced by the famous Schottky and is generally accepted in literature. Schottky's nomenclature takes only changes in relative charge of corresponding lattice, considering it to be summarily neutral, because the equation of electro neutrality is applied to the equilibrium in crystals.

1. cation in interstitial position $K\circ^{\bullet}$;
2. vacancy in cation sublattice $K\square'$;
3. anions in interstitial positions $A\circ'$;
4. vacancy in anion sublattice $A\square^{\bullet}$;
5. generated electrons Θ;
6. generated electron gaps $\oplus$;
7. sign (') reffers to negative charge;
8. sign (·) reffers to relatively positive charge of all defects;
9. $M_1\bullet^{\bullet}M_2$ incorporation of multivalent M_1 instead M_2;
10. $M_1\bullet^{\prime}M_2$ incorporation of lowervalent M_1 instead M_2;
11. $K\square^{x} \rightleftarrows K\square^{\bullet} + \Theta$ (V center of coloration);
12. $A\,\square^{x} \rightleftarrows A\square^{\bullet} + \Theta$ (F center of coloration);

The development of certain technologies puts ever more stringent demands on new materials for science. Materials science is a young scientific branch, and it represents a multidisciplinary field of chemistry, physics, mathematics, physical chemistry, solid state physics. The task of materials science can be reduced to: a) obtaining completely new materials; b) obtaining new properties of already existing materials by new procedures. In recent years, there has been a growing interest in materials based on non-stoichiometric metal oxides. It is known that superconducting ceramics, which represent one of the greatest discoveries of the 1980s, are structurally different mixtures of metal oxides. The process of titanium oxidation is thermodynamically spontaneous, its speed depends on kinetic and diffusion process parameters. According to optical measurements results, the oxide layer formed on titanium has a thickness of only 1.7 nm. A layer of this thickness is formed at room temperature within two hours, and in 40-50 days it grows to 3.5 nm, [1].

In glass-metal or metal-ceramics technology, an important role is played by previous metal oxidation, in order to replace the metal bond with an oxide one. This paper represents a modest contribution in that direction. Limitations in the spontaneous growth of TiO_2, which result in small oxide thickness (up to 5 nm), can be overcome by choosing an appropriate oxidation procedure with well-defined process parameters. In this sense, the influence of different oxidizing agents in combination with appropriate procedures of thermal oxidation of Ti - TiO_2 – oxidant system was investigated [2].

1.2 Oxidation model of Ti – TiO_2 – oxidant system

As it is known, metallic state is thermodynamically unstable and, in contact with surrounding environment, metal tends to change to a more stable ionic state in aqueous solutions or to reward stable oxides, nitrides and carbonates with air. Therefore, if a metal is in an atmosphere of oxygen or air, an oxide layer as reaction product is formed on metal surface [3]. These layers can be transparent to visible light; if they are thin enough, or to have their natural coloring, when they are thicker and more defective. The further oxidation process depends on the character of thin oxide layers that have just been created naturally. So, for example, if the oxide layer is compact and non-porous, there is a separation of the participants in the reaction with a significant reduction in oxidation rate. In this case, oxidation rate does not depend on chemical reaction rate, but rather on diffusion and migration limitation [4 – 6]. The basic oxidation model can be represented schematically as in Fig. 1.

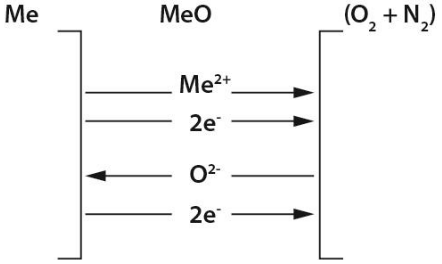

Fig. 1 – *Schematic representation of metal oxidation simplified model.*

Metal oxidation is a heterogeneous process in a gas-solid or liquid-solid system, which proceeds through a series of successive stages, of which the one that is the slowest determines overall speed of the process. As the model in Fig. 1 shows, immediately after a thin oxide layer formation, two interphase contacting surfaces are formed: Me-MeO and MeO-$O_2(N_2)$ boundaries. The main reactions at phase boundaries are as follows:

1. Oxygen dissociative chemisorption:

$$O_2 \rightleftarrows O + O\,, \tag{1}$$

$$O + e \rightleftarrows O^- \text{ (chemisorbed)}; \tag{2}$$

2. Incorporation of chemisorbed oxygen into oxide lattice with new oxyde formation:

$$O^{2-} + Me^{2+} \rightleftarrows MeO\,; \tag{3}$$

3. Metal ionization at phase boundary Me-MeO:

$$Me \rightleftarrows Me^{2+} + 2e\,; \tag{4}$$

4. Metal ions migration and diffusion through oxide layer to the reaction zone;
5. Oxide ions migration and diffusion through oxide layer to the reaction zone;
6. Electrons injection into oxide layer from the phase boundary Me-MeO.

The metal oxidation rate is a quantity that can be measured in a variety of ways. The most common way is to measure the oxide thickness as a function of time. However, oxidation rate can also be monitored by measuring mass increment (Δm) as a function of time. Depending on the process parameters and the real structure of obtained oxide film, different changes in oxidation rate with time are obtained. These changes with time are defined by corresponding functional dependencies, which, at the same time, determine the legality of oxidation process. Depending on these dependencies nature, changes in mass increment with time are distinguished by linear, parabolic, cubic and logarithmic dependencies, which are defined by corresponding dependencies:

1. Linear dependency:

$$\Delta m = K_1 t\,; \tag{5}$$

2. parabolic dependency:

$$\left(\Delta m\right)^2 = K_1 t\,; \tag{6}$$

3. cubic dependency:

$$\left(\Delta m\right)^3 = K_k t\,; \tag{7}$$

4. logarithmic dependency:

$$\Delta m = K_e \log\left(at + t_0\right). \tag{8}$$

In equations (5) – (8) Δm represents mass increment, t is time and K with corresponding indexes represents corresponding proportionality constants – oxidation process rate.

Metals, which oxidize linearly, have a high oxidation rate that is unlimited over time, so it is said that a catastrophic oxidation process applies to them. Some other metals have, on the other hand, other forms of regularity, and their oxidation rate is limited over time, because oxidation process rate can be reduced by several orders of magnitude [2, 7, 8].

Titanium and its numerous alloys oxidize according to logarithmic or parabolic dependence, depending on the process parameters. These facts indicate that there are certain limitations in the oxide growth, related to the kinetics of oxidation and the phenomena of the main and secondary charge carriers transport, as participants in the reaction. In order to change the legality of titanium oxidation process according to parabolic or para-linear mechanism, it is necessary to make significant changes in oxide layer structure, as well as the parameters and mechanism of the oxidation process [2]. With previous chemical treatment of the surface and subsequent thermal treatment, more drastic changes in the character and rate of titanium oxidation can be expected [7].

2 Experiment

2.1 Experiment program

The aim of this work is to obtain oxide coatings on titanium by chemical and thermal oxidation. It is predicted that oxidation rate will depend on titanium surface previous preparation, contamination of the surface with various impurities, choice of means for chemical oxidation and treatment time in it, temperature of thermal treatment, treatment time, composition and concentration of possibly present impurities, presence of cations of different oxidation states, as on compatibility of chemical and thermal oxidation. For the sake of economy of the whole process of thermo-chemical oxidation, it is necessary to determine the optimal parameters of this process. Since it was assumed that chemical oxidation can produce oxide coatings with a smaller thickness, the main emphasis was placed on determining the optimal parameters of thermal oxidation, i.e. temperature and time treatment.

2.2 Experimental procedure

Series of titanium tablets of dimensions 45×20×1 mm was prepared for the experimental work. Tablets are subjected to the following chemical and thermal operations and treatment:

1. Titanium samples degreasing in 10% NaOH solution for 3-5 min;
2. Titanium surface etching in a solution containing 20% HNO_3, 5% HF and 5% H_2O_2, during 1-2 min;
3. Chemical oxidation in solution containing 200 g/dm^3 $(NH_4)_2S_2O_8$ and 100 ml/dm^3 H_2O_2, during 2-5 min;

4. Thermal oxidation at temperatures of 500, 600, 700, 800 and 900°C, for a constant time of 4 hours, in the atmosphere of N_2 +O_2 (air).

One part of the samples was subjected to the following technological process, where the conditions of chemical oxidation were changed, and thermal oxidation was performed at constant temperature for different treatment times:

1. Titanium etching in a solutin containing 20% HNO_3 and 5% HF, for 20s;
2. Titanium chemical oxidation in a solutin containing 40 vol.% H_3PO_4, 56 vol.% H_2O_2, i.e. from eight volume parts of H_3PO_4 and ten volume parts of H_2O_2;
3. Titanium thermal oxidation in a the air atmosphere, at constant temperature of 900°C, for the following times: 20 min, 1, 2, 3, 4, 5, 6 hours.

3 Results of Thermo-Chemical Oxidation of Ti – Tio2 – Oxidant System

The results of titanium thermo-chemical oxidation at different temperatures, for a constant time of 4 hours, are shown in **Table 1** and graphically in Fig. 2.

Table 1

Titanium oxide coatings thickness obtained by thermo-chemical oxidation at different temperatures, for a constant time of 4 hours.

Temperature [°C]	Coating thickness [μm]			
	x_1	x_2	x_3	x_{sr}
500	49	52	50	50,3
600	79	76	76	77
700	102	107	107	105
800	121	126	124	123,6
900	149	153	150	150,6

As shown in **Table 1** and Fig. 2, it can be seen that oxide coatings thickness increases linearly with increasing temperature, starting from 50 μm at 500°C to 150 μm at 900°C. Based on this, the change in oxide layer thickness with temperature will be calculated, which is approximately 25 μm/hour.

By extrapolation of linear part to the intersection with ordinate, initial thickness of oxide coating (up to) about 40 μm is obtained, which actually represents oxide layer thickness obtained by chemical oxidation. Linear course of titanium thermal oxidation with time indicates the mechanism of catastrophic oxidation, which is a consequence of serious changes in morphology and structure of oxide layer after chemical treatment. As it is known, pure titanium

(IV) oxide is white or transparent in the form of a thin film. Main defects in undoped oxide are oxygen vacancies ($O\square^{\bullet\bullet}$) or interstitial titanium ions excess ($Ti\bullet^{\bullet}$). Thermo-chemical oxidation usually drastically increases the concentration of these defects, which are reflected in titanium oxidation kinetics. Titanium thermo-chemical oxidation is accompanied by a sharp change in oxide coating color, which can be explained by a higher concentration of oxygen vacancies. Namely, non-defective TiO$_2$ crystals are in equilibrium with the following defects [8, 9]:

$$\left(non-defective\,\mathrm{TiO_2}\right)\rightleftarrows \mathrm{O}\square^{\bullet\bullet}+2e+\mathrm{O_2}\left(gas\right). \qquad (9)$$

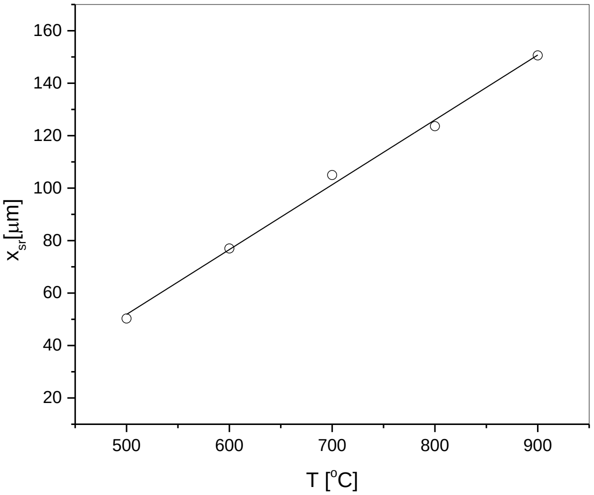

Fig. 2 – *Titanium oxide coatings thickness in function of thermal treatment temperature.*

Positively charged oxygen vacancies are compensated with the corresponding negative charge (10), so that a new defect $O\square^{x}$ – F center of coloration is formed:

$$\mathrm{O}\square^{\bullet\bullet}+2e\rightleftarrows \mathrm{O}\square^{x}. \qquad (10)$$

If light of a certain wavelength (λ) or frequency (ν) is absorbed at this center of coloration, a photoeffect occurs according to the following symbolic equation:

$$\mathrm{O}\square^{x}+h\nu\rightleftarrows \mathrm{O}\square^{\bullet\bullet}+2e. \qquad (11)$$

Since a yellow layer is formed on titanium oxide coating during catastrophic oxidation, it is likely that this oxide absorbs radiation from blue region of visible part of the spectrum.

Thicknesses of titanium oxide films obtained for different times of thermal treatment are given in **Table 2**. and Fig. 3. As can be seen from Fig. 3, oxide layer thickness changes linearly with thermal treatment time, up to a time close to 4 hours, when there is a slight curvature, i.e. a deviation from linearity. Time change of growth rate is approximately 30 μm/h, i.e. 0.5 μm/min. By extrapolation of linear part, the initial oxide film thickness, formed by chemical oxidation, is obtained. Inflection point on the curve in Fig. 3 gives optimal chemical treatment time, which is 3.8 hours.

Table 2

Titanium oxide coatings thickness obtained by thermo-chemical oxidation at different treatment times, for a constant temperature of 900°C.

Treatment time (min)	Coating thickness (μm)			
	x_1	x_2	x_3	x_{sr}
20	40	42	40	41,3
60	60	58	61	59,6
120	90	95	94	93
180	118	123	119	120
240	145	141	142	142,6
300	160	160	162	160,6
360	164	168	168	166,6

Since titanium thermo-chemical oxidation was carried out in two phases - chemical oxidation in the first and thermal oxidation in the second, the source of oxygen as an oxidizing agent changed. Chemical oxidation products and oxidizing agents excess remain on sample surface, thus participating in the initial thermal oxidation, and some ions, such as (H^+) (F^-) remain trapped in oxide structure all the time. Substitutional replacement of (O^{2-}) ions in oxygen sublattice, with H^- and F^+ ions, provokes further creation of oxygen vacancies [8]. As chemical oxidation was carried out at room temperature, and treatment time was relatively short, an oxide layer of small thickness was obtained. Chemical oxidation process is completely under kinetic control, because oxygen diffusion through thin and chemically etched oxide is not a limiting factor. It should be emphasized that oxygen diffusion through oxygen gaps is followed up by ions migration by a strong electric field, which is established between adsorbed oxygen layer (O^{2-}hem) at TiO_2 phase boundary and positively charged (Ti^{4+}) ions accumulated at Ti-TiO_2 phase boundary. However, oxidation front was moved closer to TiO_2-O_2 phase boundary, due to higher diffusion rate of (Ti^{4+}) ions. Thermal oxidation, which follows after chemical oxidation, is characterized by an increased temperature and significantly longer treatment time. Oxygen source is ambient air in oxidation furnace, and slow process may be oxygen diffusion from gas stream core toward oxide surface. However, thicker oxide coatings are still an obstacle for smooth continuation of oxidation process, so the regularity changes from linear to parabolic, that is, to para-linear regularity (Fig. 3).

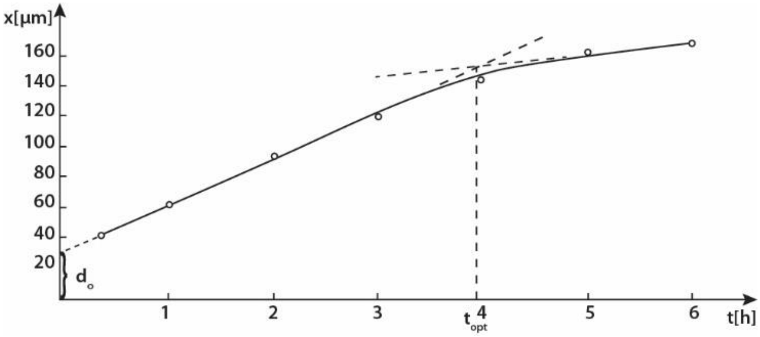

Fig. 3 –*Titanium oxide coatings thickness in function of thermal treatment time, at the constant temperature of* 900°C.

4 Discussion

Introduction to the physical aspects of disorder – defects generation and electrical carriers transfer in Ti – TiO_2 – oxidant system

According to Wagner's theory of oxidation, oxidation process kinetics is mainly defined by: charge carriers transfer through metal - oxide layer - medium (MOS) system and oxidation reaction free energy change. In this sense, oxidizing metal - oxidant system is represented as an electrolytic cell in which metal and oxygen are electrochemically active substances, and oxide layer is simultaneously an electrolyte and an electron conductor [10 – 12]. Therefore, since it is a solid electrolyte (disordered TiO_2), charge carriers mobility plays an important role in oxidation process. In such complex systems with significantly accelerated oxidation processes, electrical conductivity is conditioned by electrons and ions transfer in Ti – TiO_2 – oxidant system, through damaged and defective TiO_2 structure with point electronic defects. Concentration or number of these defects in TiO_2 structure is equivalent to the number of oxygen vacancies ($O\square^{\bullet\bullet}$) or interstitial positions ($Ti\circledast^{\circledast}$), whose transfer is significantly slower than the real electron transfer. Precisely for these reasons, a barrier appears due to concentration gradient and changes in created layer (TiO_2) electronic and ionic conductivity ratio, whose thickness is several hundred times greater than the natural oxide layer (166 µm vs. 3.5 nm).

Overall, there are two types of disorder in TiO_2. Metal excess (Ti) is realized in two ways: through vacancies in the oxygen sublattice ($O\square^{\bullet\bullet}$) and through interstitial positions ($Ti\circledast^{\circledast}$), according to following reactions [4]:

$$1.\quad \mathrm{TiO_2}\left(non-defectivecrystal\right) \rightleftarrows \mathrm{O}\square^{\bullet\bullet} + 2\odot + \tfrac{1}{2}\mathrm{O_2}\left(g\right), \tag{12}$$

$$2.\quad \mathrm{TiO_2}\left(non-defectivecrystal\right) \rightleftarrows \mathrm{Ti}{\bullet}^{\bullet} + \odot + \mathrm{O_2}\left(g\right), \tag{13}$$

Both disorders indicate n-type conductivity of TiO_2. Conducting electrons density at (–190°C) is 10^{17} to 10^{18} el/cm^3, while at a temperature of 500°C, electrons concentration suddenly increases by about 100 times, but their mobility is relatively low [9]. Precisely because of charges lower mobility in disordered and defective oxide layer in oxidation process, concentration gradients occur at $Ti-TiO_2$ and TiO_2 – oxidant phases boundaries. In natural thin oxide layer TiO_2, due to scale effects in nano and micro thin layers, electronic conductivity is completely dominant. Nano and micro oxide layers are ionically almost non-conductive. In this work, a new accelerated oxidation procedure was applied in Ti – TiO_2 – oxidant system, by choosing oxidant and process temperature. Extremely fast oxidation processes, with a huge number of oxygen vacancies ($\mathrm{O}\square^{\bullet\bullet}$) and interstitial ions create conditions for good ionic conductivity. In addition to these defects, sudden oxidation also causes amorphization of TiO_2 oxide layer, which is more suitable for ionic and electronic conductivity in a favorable mutual relationship, so that the usable value of sudden oxidation process is accomplished.

Ionic and electronic conductivity ratio can be changed by doping - by incorporating active impurities into the oxide layer ($M_1{\bullet}^{\bullet}M$) (M_1 instead of M), for example:

$$\mathrm{WO_3} \rightleftarrows \mathrm{W}{\bullet}^{\bullet\bullet}\left(\mathrm{Ti}\right) + 2\odot + \tfrac{1}{2}\mathrm{O_2}\left(g\right), \tag{14}$$

$$\mathrm{WO_3} + \mathrm{O}\square^{\bullet\bullet} \rightleftarrows \mathrm{W}{\bullet}^{\bullet\bullet}\left(\mathrm{Ti}\right) + 2\odot + \mathrm{TiO_2}. \tag{15}$$

On the other hand, by adding Cr_2O_3 – trivalent (Cr) incorporated into tetravalent (Ti) (TiO_2), we have:

$$\mathrm{Cr_2\,O_3} \rightleftarrows 2\,\mathrm{Cr}{\bullet}'\left(\mathrm{Ti}\right) + \mathrm{O}\square^{\bullet\bullet} + 2\,\mathrm{TiO_2}. \tag{16}$$

Thus, in the presence of WO_3, electronic and ionic conductivity increases, thermo-chemical oxidation is accelerated due to O_2 and electrons excess, and in the presence of Cr_2O_3 according to (16), oxygen gaps increase, but oxygen decreases (it is consumed). In any case, incorporation of other multivalent oxides into TiO_2 increases ionic conductivity, which would be beneficial in the use of these systems as electrolytes for accumulators and batteries.

Any of crystalline TiO_2 periodicity disruption results in creation of sufficiently deep potential gaps on underlying periodic crystal, which can capture and trap charge carriers. State of an electron captured by such a potential barrier is called local state according to quantum theory of amorphous conductors. Of course, oxide layer crystallinity disruption is process that leads to oxide layer (TiO_2) amorphization and many other treated oxides. Local levels are associated with local states of defects or impurities [8 – 12], so such states can be called impurity states. The number of such states is from 10^{18} to $10^{20}/cm^3$.

Due to the specificity of extremely fast oxidation processes, which were applied in this original and unique work, it is normal to expect above-mentioned concentrations of impurity states. Of course, the higher the concentration of defects or impurities, the greater the activity of Ti – TiO_2 – oxidant system. It is worth emphasizing, for the sake of general knowledge transfer, that the purest crystalline materials without significant interventions have from 10^{12} to 10^{14} defective and impurity states per cm^3, which means that it is not possible to obtain a crystal purer than $10^{12}/cm^3$, which limits numerous technologies in semiconductors and dielectrics.

For an amorphous oxide state or a partially amorphized state in which there is no larger-range periodicity, electron free path mean length is observed as a classical transfer, with a series of jumps from one state to another. As a result of the jump, at each instant of time the electron is localized around one state or defect. Therefore, there are no continuous transitions, but discrete transitions, whose transfer – leap requires greater kinetic energy. As a consequence of this electrons state, there is a noticeable decrease in conductivity in amorphous materials [8, 12].

Nature of Ti – TiO_2 and TiO_2 – oxidant contact is of special importance when it is about natural oxidation of Ti – TiO_2 – medium (O_2) system and when the system has a low n-type conductivity. In relatively pure TiO_2, due to large width of forbidden zone, free charge carriers are absent or their density is negligible. In such cases, conductivity can be controlled by injection - injecting charge carriers into TiO_2. However, in real TiO, due to thermal oscillations of certain bonds in the lattice, as well as the presence of neutral or charged impurities and structural defects, turbulent process of thermo-chemical oxidation of Ti – TiO_2 – oxidant system leads to continuous scattering or charge carriers capture. The tendency is that violent oxidation processes create capture centers and structural defects in oxide layer, as already stated, in concentrations close to 10^{18} to $10^{20}/cm^3$. Captured charge carriers in dielectric TiO_2 do not conduct electricity, because they directly build up the Debye space charge, reducing total current by acting as a blocking contact [8]. In a word, the mechanism of charge carriers transfer through a dielectric layer limited by space charge is complex.

This phenomenon is interesting because it is based on consideration of Ti – TiO_2 – M system, known under the term dielectric diode. It is worth pointing out that this work has a usable value. This type of diode has very good rectification properties of magnitude order 10^6 and particular application at higher temperatures above 500°C [9].

5 Conclusions

Natural titanium oxide layer, obtained by spontaneous thermodynamic process, is a very thin oxide film with nano dimensions of 1.7 to 3.5 nm. Such a thin oxide layer is an n-type semiconductor, with negligible ionic conductivity. $Ti - TiO_2$ – oxidant composite system has an increased degree of disorder from 10^{18} to $10^{20}/cm^3$. By thermo-chemical oxidation of TiO_2 oxide layer accelerated growth, an oxide layer of high activity was obtained due to significantly increased concentration of oxygen vacancies ($O\square^{\bullet\bullet}$) and substitutional titanium defects ($Ti{\bullet}^{\bullet}$) by several hundred times, compared to natural oxidation. High concentration of positive space charge significantly increases TiO_2 conductivity. Thick oxide coating on titanium, obtained by thermo-chemical oxidation of $Ti - TiO_2$ – oxidant system, with the chosen technology and work methodology, represents a good basis for performance of composite materials $Ti - TiO_2$ – glass, $Ti - TiO_2$ - ceramics, $Ti - TiO_2 - MO$ and $Ti - TiO_2 - M$ (M refers to some other metal). A special application of accelerated oxidation thermo-chemical process (catastrophic oxidation) is to obtain an active dielectric diode $Ti - TiO_2 - M$ (M is evaporated metal) with extremely high rectification properties, 10^6 times, for exploitation at high temperatures above 500°C, where it is not possible to apply diodes based on the p-n junction of semiconductors. Electroconductivity of $Ti - TiO_2$ – oxidant system has been achieved by successive electron jumping. Favorable electronic and ionic conductivity ratio is the basis for the future solid electrolyte. This system possesses significantly increased oxide layer thickness compared to the natural one by several hundreds of times, and also extremely fast oxidation process with a huge number of oxygen vacancies ($O\square^{\bullet\bullet}$) and interstitial defects ($Ti{\bullet}^{\bullet}$) ions. Hexavalent and trivalent oxides accelerate – increase thermo-chemical oxidation effects. The state of an electron trapped in potential wells is called local state with local levels. Local levels are associated with local states and can be called impurity states according to quantum theory. Using thermo-chemical method, a quite thick oxide coating on titanium can be obtained in a relatively short time. Obtained oxide coating consists mainly of TiO_2, and at temperatures above 900°C there is a possibility for the oxynitride and nitride formation. Created oxide film is deficient in oxygen, so TiO_2 belongs to n-type semiconductors. Oxidation rate is constant in temperature interval 500–900°C and treatment time 0 – 4 hours.

6 Acknowledgement

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