EFFECT OF OXYGEN NONSTOICHIOMETRY OF CERAMIC TARGETS ON DEPOSITION PROCESS OF TiO_2 BY DC MAGNETRON SPUTTERING

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The deposition of stoichiometric TiO_2 films for V_2O_5/ TiO_2 catalysts was investigated. DC magnetron sputtering from ceramic oxide targets in an argon/oxygen atmosphere was chosen as deposition technique. Ceramic TiO_{2-x} targets with a wide range of oxygen nonstoichiometry were prepared following a standard ceramic procedure starting from TiO_2 and Ti powders. The effect of oxygen nonstoichiometry on target behaviour upon sputtering was followed by means of the target voltage. Increase of voltage maximum with increasing nonstoichiometry of ceramic target was observed and discussed. Optical properties of layers prepared with different oxygen concentrations in the plasma were investigated.

1. INTRODUCTION

Titanium oxide (TiO_2) has a number of attractive properties, which include high refractive index, high dielectric constant, semiconductor properties and chemical stability. These properties make it suitable for a range of applications such as antireflective and protective layers for optical coatings, UV filters, oxygen or humidity sensors including photocatalysts for the air oxidation of organic compounds [1-2] and solar energy conversion [3].

TiO_2 films have been prepared by a variety of deposition techniques such as the sol-gel process [4], chemical vapour deposition [5], evaporation [6], various reactive sputtering techniques [7-8], ion beam assisted process [9], atomic layer deposition [10], pulsed laser deposition [11] and filtered arc deposition [12]. Among these techniques, the popularity of DC reactive sputtering from elemental (metal) targets can be attributed to several factors like good coating uniformity, high purity and good film adhesion. However, opera-

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tion with a metal target implies several drawbacks in the reactive mode, such as process instability and low deposition rates [13]. Transparent, i.e. stoichiometric layers of TiO_2 are only obtained when sputtering in the oxide mode, i.e. with a high O_2 partial pressure. In this mode the target surface is highly oxidized, giving rise to arcing while within the race track a modified surface layer is created, which leads to a lower sputter yield and a correspondingly lower deposition rate. Higher sputter rates can be obtained when operating in the transition mode, closer to the metallic mode (i.e. low O_2 partial pressure), but this is a highly unstable operation zone which needs continuous feed back control e.g. by means of a plasma emission monitor (PEM) and controllable and fast reacting valve for O_2 introduction. Moreover, in this regime and in order to obtain stoichiometric layers, the substrate-to-target distance has often to be increased, so that Ti and O or O_2 particles, either neutral or ionised, reach the substrate in the ratio necessary for stoichiometric deposition [14]. In other words, a substrate-to-target distance such that the sputtered and deposited Ti has the time to react with the oxygen available at the substrate. All of these measures are technically complicated and make it worthwhile exploring stoichiometric deposition from oxide targets. Oxide targets can indeed be used in DC operated magnetrons, provided they are reasonably electrically conducting. Conductivity of TiO_2 ceramics is directly related to its oxygen nonstoichiometry. In this work ceramic TiO_{2-x} targets with a different conductivities were prepared by changing Ti:O ratio and the effect of their nonstoichiometry on deposition of stoichiometric TiO_2 layers was studied.

2. EXPERIMENTAL

TiO_2 rutile powder (type 3025, Kronos, Germany) was used for preparing titanium oxide targets. To change Ti:O ratio, 0-70wt% of titanium metal powder (99.6% Ti, grain size of 32 μm, Aldrich) was added to rutile powder and compositions were homogenized 24h in a ball mill in ethyl alcohol. The mixed powders were cold pressed and then sintered at 1700°C for 1h in vacuum (target prepared from pure TiO_2 powder) or hot pressed at 1700°C for 1h in argon atmosphere (composite targets). This preparation was done in the Institute of Electronic Materials Technology (IEMT, Warsaw). Sintering in vacuum ($1.3x10^{-4}$ Pa) of typically white titania powder resulted in black targets. XRD (Siemens Diffractometer Kristalloflex D5000) revealed that the only phase present is rutile (Tabl. 1). Targets prepared from the mixed powders were brown, golden or metallic in colour dependent on metal titanium powder content. Phase composition analysis pointed out the presence of titanium suboxides: Ti_2O_3 TiO and Ti_2O. Rutherford Backscattering Spectrometry (RBS)

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measurements showed that the resulting composition of the titanium oxide targets changed with titanium content in initial powder composition from $TiO_{1.75}$ to $TiO_{0.5}$. RBS measurements were taken with a 2MeV He^{+4} beam produced by the Van de Graaff accelerator of the IEMT (Warsaw). Van Der Pauw type measurements yielded target resistivities of 0.7-0.00026 Ωcm. For comparison pure titanium target was also used.

Table 1. XRD and resistivity measurement results of composite titanium oxide targets.

Powder composition, wt%		Phase composition of target	Resistivity, κ, Ωcm	x in formula TiO_{2-x}
TiO_2	Ti			
100	0	**TiO_2 (rutile)**	0.7	0.25
80	20	**Ti_2O_3 (50%), TiO (50%)**	0.0065-0.003	0.75
65	35	**TiO**	0.001-0.0008	1.0
50	50	**TiO (mainly), Ti_2O (small amount)**	0.0005-0.00026	1.2
30	70	**Ti_2O**	0.0005-0.00026	1.5

Depositions were performed from 6 mm thick targets with a diameter of 50mm onto unheated glass substrates. The substrate-target distance was 100 mm. The magnetron-sputtering source was operated by means of a Hüttinger power supply (PFG 1500 DC). Before deposition the chamber was pumped down by a rotation pump (Balzers DUO100) and diffusion pump (Balzers DIF320, BFA 320 W baffle) to a base pressure of $1x10^{-3}$Pa. The pressure was measured by Pirani and Penning pressure gauges. Sputtering gases Ar and O_2 were introduced through stainless steel tubes at the top of the system and standard mass flow controllers (AERA ROD4) controlled both flows. The input power was set at 100 W. The power density at the ceramic target determined from the size of the race track was 7 W/cm^2. Each reactive sputter deposition was preceded by target sputter cleaning in pure argon.

The layers were characterised optically by means of specular transmission measurements (Varian Cary 5), from which absorption coefficient α was determined.

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3. RESULTS AND DISCUSSION

As it occurred, all ceramic targets independent of Ti:O ratio (and their conductivity) are working in the same range of argon sputtering pressure – 2-8x10^{-2}mbar (Fig.1). For comparison metallic titanium target is sputtered at really lower pressures (Fig.2). However the maximum of deposition rate from ceramic targets observed at 15sccm argon flow increases with increasing oxygen nonstoichiometry (Fig.3). Such dependence seems to be obvious, because with decreasing oxygen content, ceramic targets are getting more and more metallic in character which results in higher deposition rate. For all ceramic targets, the deposition rate decreases with increasing argon flow (Fig.4).

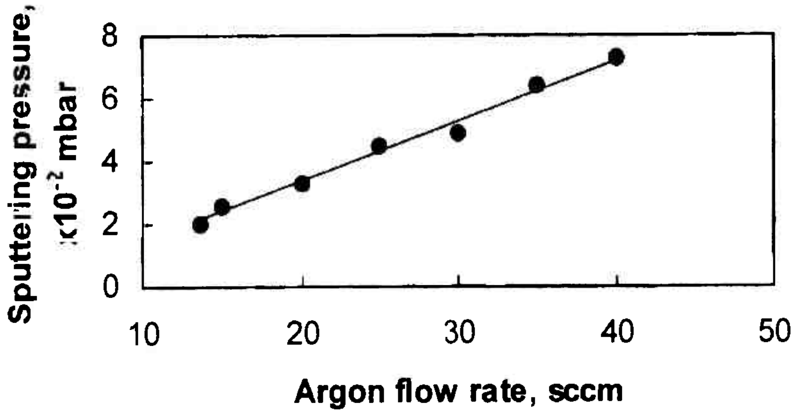

Fig.1. Sputtering pressure for ceramic TiO_{2-x} targets as a function of argon flow rate.

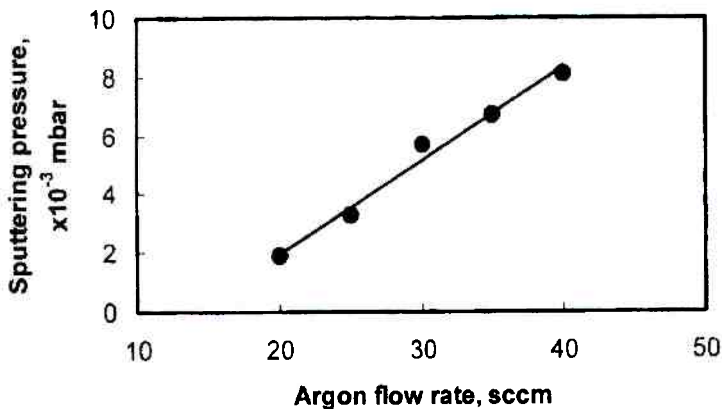

Fig.2. Sputtering pressure for pure titanium target as a function of argon flow rate.

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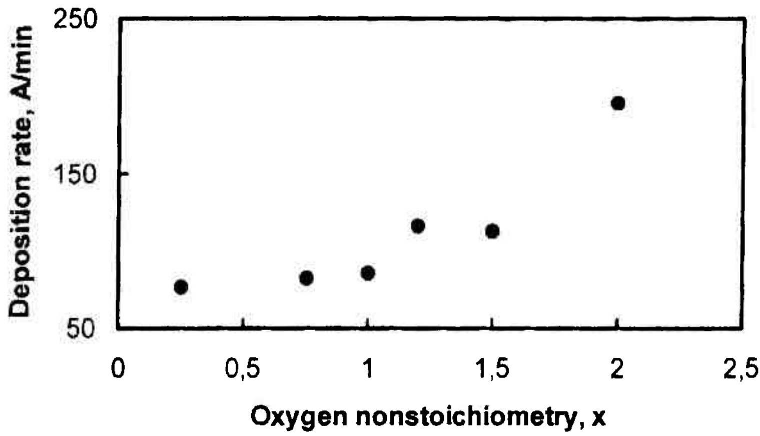

Fig.3. Maximum deposition rate as a function of oxygen nonstoichiometry of ceramic targets.

x=0.25

x=0.75

x=1.0

x=1.2

x=1.5

Deposition rate, A/min

Argon flow rate, sccm

Fig.4. Deposition rate of TiO_{2-x} layers from ceramic targets as a function of argon flow rate(in the frame oxygen nonstoichiometry, x, of ceramic targets is given).

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As the chamber pressure varied linearly with argon flow (Fig.1), the observed decrease in deposition rate seems to be a result of some opposite effects. First of all, increasing the argon sputter pressure results in a smaller mean free path of the sputtered species and consequently they are more scattered. Increasing the argon pressure will also result in more volume ionisation. This will reduce, at constant power, the target voltage, i.e. the ion energy and will increase the total current, or stated differently more ions will bombard the target surface. Another effect which can influence the deposition rate is the reduction of target surface due to argon ion bombardment. As it was found from our XPS measurement the surface of TiO_{2-x} target is reduced by argon ion bombardment due to preferential oxygen sputtering and the bombarded surface changes to metal rich comparing to original surface. In the case of pure metal target where no reduction of target surface occurs linear decrease of deposition rate is observed (Fig.5). It seems to be a result of increasing argon sputtering pressure, only.

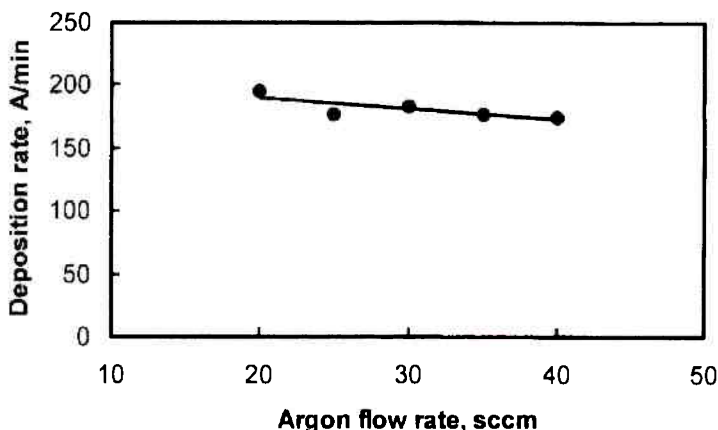

Fig.5. Deposition rate of Ti layers from titanium target as a function of argon flow rate.

Sputtering voltage also decreases with increasing argon flow during sputtering of ceramic TiO_{2-x} targets (Fig.6). As can be seen, this dependence appears to be linear. The slope a (Tabl. 2), which can be interpreted as sputtering voltage decrease rate per argon flow unit, does not differ significantly going through all ceramic targets. It can mean that the slope is independent of target stoichiometry. The same determination made for pure titanium target shows the slope *a* is really lower. The difference in slope can be related to the secondary electron emission from oxide components, which is generally higher then their metal constituents.

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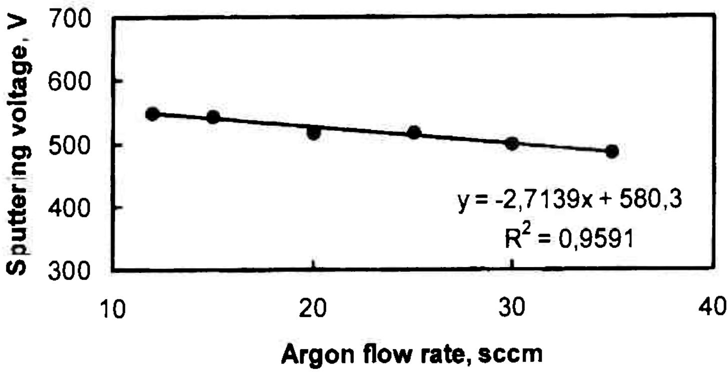

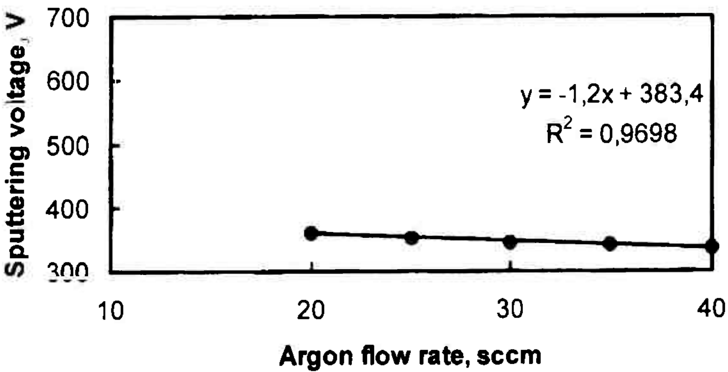

Fig.6. Sputtering voltage as a function of argon flow rate for ceramic target with x = 0.25 (top scheme) and metallic target (bottom scheme).

Table 2. Average value of slope parameter *a* as a function of target nonstoichiometry.

Target nonstoichiometry, x	0.25	0.75	1.0	1.2	1.5	2.0 (titanium target)
Slope *a*	-2.69	-2.44	-2.82	-2.80	-2.74	-1.70

As it was said earlier transmission measurements were used to calculate the absorption coefficient α of TiO_{2-x} layers at 55 nm wavelength. The minimum absorption (Fig.7) is observed for the layers obtained from target with the smallest parameter of nonstoichiometry, x. Due to target oxygen deficiency; in

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pure argon translucent water-like layers were deposited from targets with x from the range 0.25 - 1.0. For x higher than 1.0, all layers were totally black and not translucent.

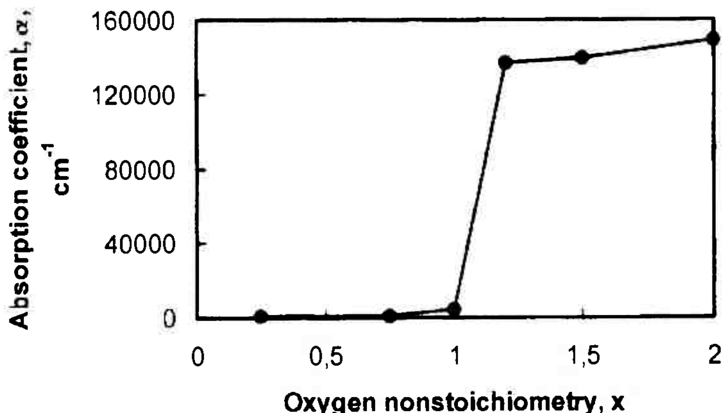

Fig.7. Absorption coefficient α of TiO_{2-x} layers prepared from ceramic target as a function of target nonstoichiometry x.

When oxygen is added to the sputtering atmosphere translucent and stoichiometric titania layers are obtained from all ceramic targets and metallic one as well. However the minimum absorption coefficient α was found moving with increasing oxygen nonstoichiometry of ceramic targets to higher oxygen content in plasma (Fig.8). Further increasing the oxygen mole fraction yielded higher absorption coefficient for all ceramic targets and as it was found earlier [15], higher oxygen deficiency of TiO_2 layers. The origin for these observations must be sought in negative oxygen ion bombardment of the substrate. As shown by Zeuner et al. [16], electron attachment of oxygen atoms in the bulk plasma is not relevant in the context of negative ion bombardment. However, negative ions formed at the target surface during reactive sputtering are accelerated away from the cathode [16-18]. Further away, as it was found by Tachibana et al. [19], Ti and O-related species ejected from TiO_{2-x} target reach the substrate with rather low energies, but oxygen must be supplied from the sputter gas for filling up the oxygen lack in order to obtain stoichiometric TiO_2 films. Part of the O_2 sputter gas is decomposed and changed to O^- ions in the plasma and these are accelerated by the electric field around the target. Upon reaching the deposited film, the negative ions cause damage to the layer because the higher penetration depth. Substrate bombardment by these negative ions will reduce the oxygen content due to preferential sputtering of oxygen atoms from the deposited layer [16]. As the oxygen content in the plasma

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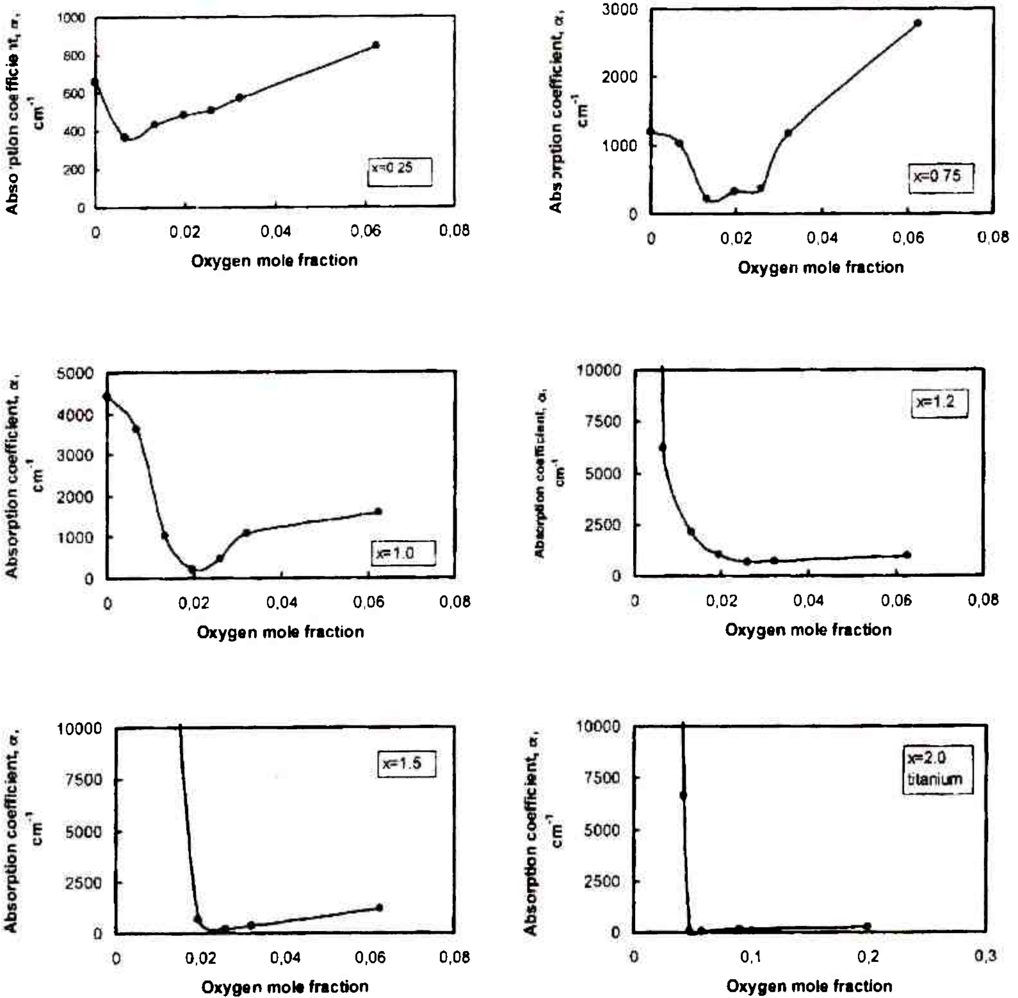

Fig.8. Absorption coefficient α of TiO_{2-x} layers prepared from all targets: ceramic and metallic, as a function of oxygen flow rate (in the frame oxygen nonstoichiometry, x, of ceramic targets is given).

increases, the target surface becomes more oxidised and more negative ions will be produced. Hence, the observed changes in film stoichiometry with the oxygen mole fraction in the plasma, is the result of two competing effects. On the one hand, addition of oxygen to the chamber results in a decrease of the deposition rate and an enhanced oxidation of the deposited layer. On the other hand, at higher oxygen concentration in the plasma, negative oxygen ion bombardment will preferentially sputter the oxygen atoms from the deposited layer.

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When oxygen is added to the sputtering atmosphere instead of increasing the argon pressure, the deposition rate is seen to decrease, when the oxygen flow rate is increased (Fig.9). However this decrease is the stronger, the higher is nonstoichiometry of ceramic target (Fig.10). This phenomenon can be related to the change of sputtering mode with increasing nonstoichiometry of targets from oxide to more metallic one. For ceramic target with x = 1.5 and pure titanium, a delay of sudden drop of deposition rate is observed due to oxygen consumption made by oxygen gettering at chamber walls.

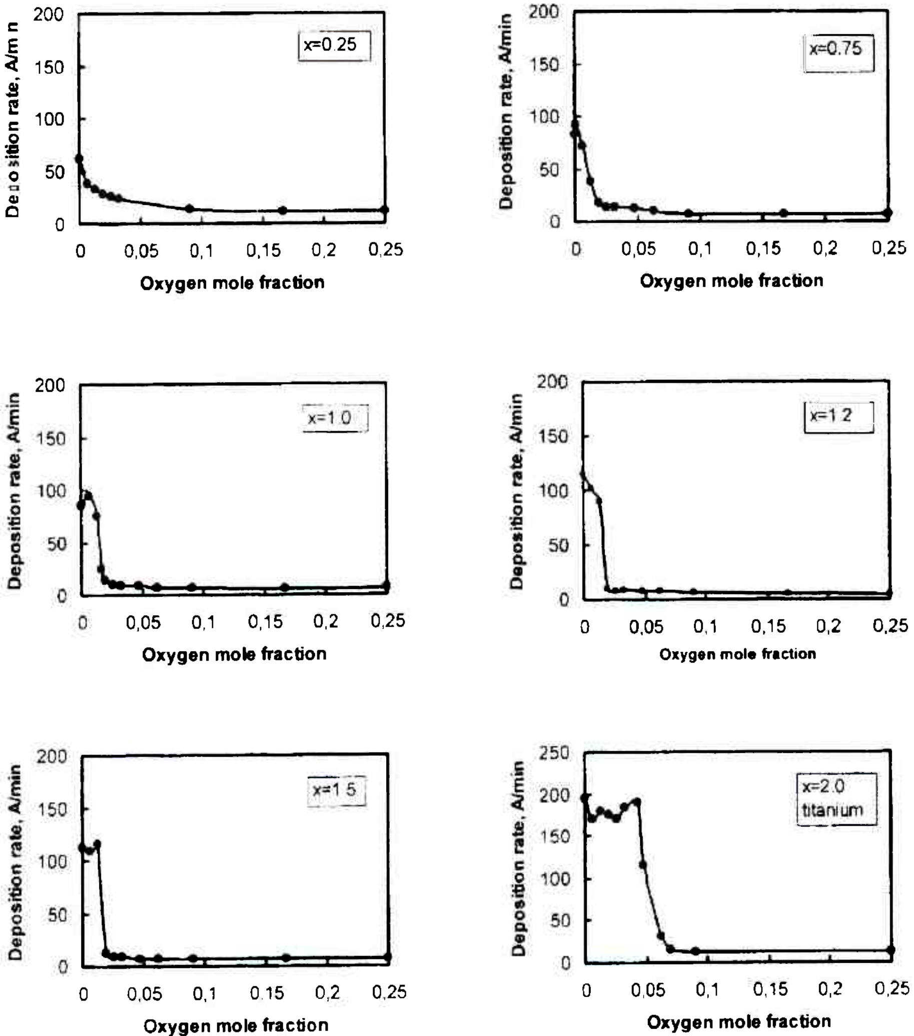

Fig.9. Deposition rate of TiO_{2-x} layers from all targets; ceramic and metallic, as a function of oxygen concentration (in the frame oxygen nonstoichiometry, x, of ceramic targets is given).

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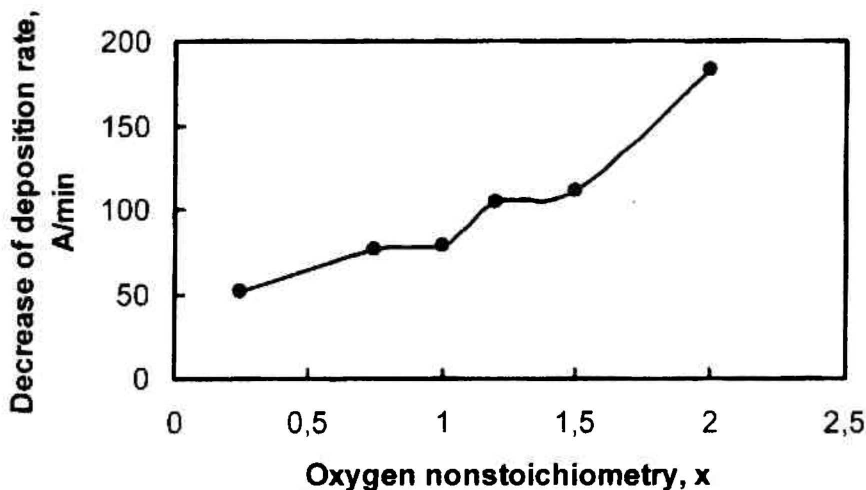

Fig.10. Decrease of TiO_2 layer deposition rate due to oxygen presence in sputtering atmosphere as a function of nonstoichiometry of target.

The influence of oxygen addition to sputter atmosphere on target voltage was also found (Fig.11). In contrast to sputtering pressure increase, which leads to a target voltage decrease, the target voltage on oxygen addition for all ceramic targets first increases. This voltage increase (Fig.12) increases with increasing nonstoichiometry of ceramic targets. Further increasing the oxygen flow rate leads to a significant decrease of the sputtering voltage. This latter decreasing part is probably related to an increasing sputtering pressure, combined with an oxidation of the target surface, which will enhance the ion induced secondary electron emission from the target. The origin of the increasing part of the voltage pattern however is still remaining unexplained. Looking at Fig.12, it seems to us that reoxidation of the targets with increasing natural oxygen nonstoichiometry should be one of the parameters responsible for the observed voltage increase. It is also easy to find that oxidation of target should reduce the ceramic target potential because of the higher ISEE of oxides. The same phenomenon, target voltage increase with initial oxygen flow rate increase, was also observed for pure titanium target (Fig.13). This increase (ΔV = 76 V) is however smaller than the same increase for the most nostoichiometric ceramic target.

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Fig.11. Sputtering voltage as a function of oxygen concentration in plasma at a constant argon flow rate (15 sccm) for all ceramic targets (in the frame oxygen nonstoichiometry of target is given).

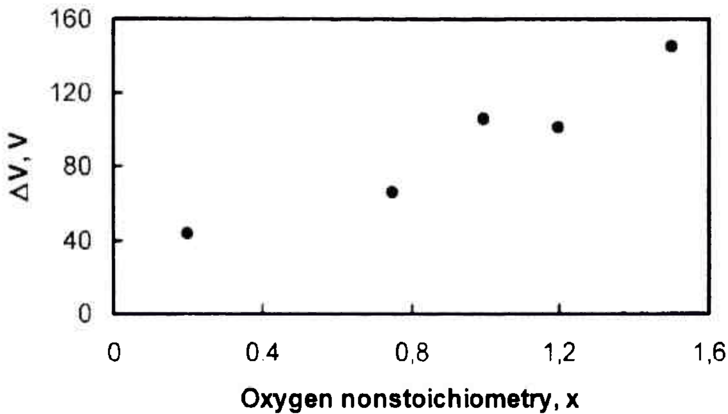

Fig.12. Increase of sputtering voltage, ΔV, on oxygen addition as a function of oxygen nonstoichiometry, x, of ceramic target.

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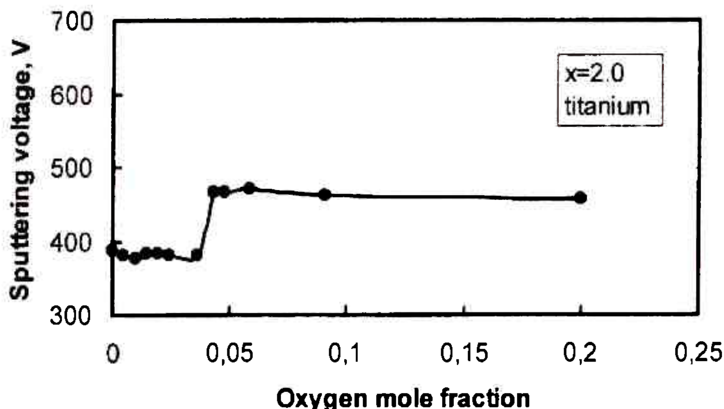

Fig.13. Sputtering voltage as a function of oxygen concentration in plasma at a constant argon flow rate (20 sccm) for titanium target.

4. SUMMARY

TiO_2 thin films have been deposited by DC magnetron sputtering, using ceramic TiO_{2-x} targets with oxygen nonstoichiometry x in the range of 0.25-1.5. Nearly stoichiometric layers were obtained with a small amount of oxygen in the sputtering gas. The amount of oxygen added necessary for filling up the oxygen lack increased with nonstoichiometry of targets. The influence of oxygen addition on sputtering voltage was found. Increase of voltage maximum with increasing nonstoichiometry of ceramic target was observed and discussed.

5. REFERENCES

[1] Ikezawa S., Mutsuga F., Kubota T., Suzuki R., Baba K., Koh S., Yoshioka Y., Nishiwaki , Kida K., Ninomiya Y. Wakita K.: *Vacuum*, 59 (2-3) (2000) 514-521

[2] Nakamura M., Aoki T., Hatanaka: *Vacuum*: 59 (2-3) (2000) 506-513

[3] Graetzel M.: *Comments Inorg. Chem.*, 12 (1991) 93-102

[4] Sabate J., Anderson M.A., Kikkawa H., Xu Q., Cervera-March S., Hill C.G. Jr: J. Catal., 134 (1992) 36-42

[5] Fujii T., Sakata N., Taakada J., Miura Y., Daitoh Y., Takano M.: *J.Mater.Res.*, 9 (1994) 1468-1473

[6] Ben Amor S., Baud G., Besse J.P. Jacquet M.: *Thin Solid Films*, 293 (1997) 163-172

[7] Okimura K., Shibata A., Maeda N., Tachibana K., Noguchi Y., Tsuchida K.: *Jpn.J.Appl.Phys.* 34 (1995) 4950-4958

http://rcin.org.pl

[8] Aarik J., Aidla A., Kiisler A., Uustare T., Sammelselg V.: *Thin Solid Films*, 305 (1997) 270-276

[9] Yoon H.S., Kim S.K., Im H.S.: *Bull.Korean Chem.Soc.*, 18 (6) (1997) 641-648

[10] Zhang F., Wang X.. Li C., Wang H., Chen L.. Liu V.: *Surf.Coat.Technol.* 49 (1998) 136-142

[11] Martin P.J., Netterfield R.P.. Kinder V.: *Surf. Coat. Technol.*, 49 (1991) 239-246

[12] Netterfield V, Martin P.J., Sainty W.G., Duffy R.M., Pacey C.G.: *Rev.Sci.Instrum.* 56 (1985) 1995-2001

[13] Szczyrbowski J., Brauer G., Ruske M., Teschner G., Zmelty A.: *J. Non-Cryst. Solids*, 218 (1997) 262-266

[14] Schiller S., Heisig U., Steinfelder K.. Strümpfel J.: *Thin Solid Films*, 63 (1979)

[15] Tomaszewski H., Poelman H., Depla D., Poelman D., De Gryse R., Fiermans L., Reyniers M. F., Marin G.: *Vacuum*, 68 (2003) 31-38

[16] Zeuner V, Neumann H. , Zalman J., Biederman H.: *J. Appl. Phys.*, 83 (1998) 5083

[17] Aita K.: *Critical Reviews in Solid State and Materials Science*, 23 (1998) 205

[18] Tucek J.C.. Walton S.G., Champion R.L: *Phys. Rev.* B, 53 (1996) 14127

[19] Tachibana Y.. Ohsaki H., Hayashi A.. Mitsui A., Hayashi Y.: *Vacuum*, 59 (2000) 836-843

[20] Kester D.J., Messier R.: *J. Mater. Res.* 8 (1993) 1928

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