Effect of hydrogen on sputtering discharge and properties of TiO$_2$ films

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This article reports on the effect of hydrogen addition into the Ar+O$_2$ discharge mixture on the dc reactive magnetron sputtering process and on the structure of sputtered TiO$_2$ films. The hydrogen plays a key role in reactive sputtering of electrically insulating oxides from metallic targets because it fully eliminates arcing on the sputtered target. The hydrogen also strongly influences the dependence of the partial pressure of oxygen p$_{O2}$ vs. flow rate of oxygen ϕ_{O2}. Changes in the p$_{O2}$=f(ϕ_{O2}) dependence caused by the addition of H$_2$ into the Ar+O$_2$ mixture are explained. Special attention is devoted to correlations between deposition parameters, structure, phase composition, optical properties and hydrophilic activity of TiO$_{x\approx2}$ films. It is shown that the presence of H$_2$ in the Ar+O$_2$ mixture does not prevent from the formation of superhydrophilic TiO$_{x\approx2}$ films.

1. Introduction

In recent years, a considerable interest is concentrated on the formation and investigation of oxide films because they exhibit some unique properties which can be utilized in many applications, e.g. as transparent electrically conductive electrodes, protective coatings with oxidation resistance above 1000°C [1] or functional surfaces with hydrophilic, self-cleaning and/or antibacterial function induced by UV light [2]. Usually, the reactive magnetron sputtering of a pure metallic target is used for the production of oxide films. This method is very convenient for large area deposition of oxide films but it suffers from arcing on the target during sputtering process in the case if the oxide is electrically insulating. The arcing occurs due to incomplete erosion of the whole target surface and charging of uneroded areas due to their conversion from electrically conductive into electrically insulating areas in the presence of oxygen in sputtering gas [3,4].

Unfortunately, many oxides of practical importance are electrically insulating and thus the development of an arc-free dc reactive magnetron sputtering is a serious task to be solved. There are, at least, two ways to avoid arcing: (1) the use of pulsed reactive magnetron sputtering [4-6] and/or (2) the addition of hydrogen into Ar+O$_2$ sputtering gas mixture [7]. At present, both methods are under an intense investigation. This article reports on the effect of H$_2$ addition into Ar+O$_2$ mixture on (i) the dc reactive magnetron sputtering process and (ii) the structure, optical and hydrophilic properties of TiO$_{x\approx2}$ thin films.

2. Experimental

TiO$_2$ films were sputtered using a dc unbalanced magnetron equipped with Ti (99.5) target of 100 mm in diameter and electromagnet in the Ar+O$_2$+H$_2$ sputtering gas mixture. Films were sputtered on unheated glass (26x26x1 mm^3) substrates under the following deposition conditions: discharge current I$_d$=3A, substrate-to-target distance d$_{S-T}$ = 100mm, total pressure p$_T$ = p$_{Ar}$ + p$_{O2}$ + p$_{H2}$ = 0.9, 1 and 1.5Pa and different values of partial pressure of oxygen p$_{O2}$ and hydrogen p$_{H2}$. Typical thickness h of TiO$_2$ films was ~1000nm. More details are given in the reference [7].

The film thickness was measured using a Dektak 8 Profilometer. The film structure was characterized by X-ray diffraction (XRD) using PANalytical X'Pert PRO diffractometer working in Bragg-Brentano geometry using a CuKα (λ=0.154187 nm). The hydrophilicity of the surface of TiO$_2$ films was characterized by a water droplet contact angle (WDCA) α_{ir} after irradiation by the UV light (Philips TL-DK 30W/05, W$_{ir}$=0.9mWcm^{-2}, λ=365 nm) measured by a Surface Energy Evaluation System (made by the Masaryk University in Brno, Czech Republic). Optical properties (transmission and absorption were measured by the spectrometer Specord M400 (Carl Zeiss Jena, Inc., Germany). The optical bandgap energy E$_g$ was evaluated from measured UV-vis spectra using a Tauc plot.

3. Results
3.1. Sputtering discharge

The addition of H$_2$ into Ar+O$_2$ sputtering gas mixture strongly influences the sputtering discharge, see Fig.1. In the metallic mode of the sputtering discharge burning in Ar+O$_2$ mixture all oxygen is gettered by sputtered Ti atoms and at the Ti target surface (p$_{O2}$=0). On the contrary, p$_{O2}$ starts to linearly increase in the metallic mode when H$_2$ is added into Ar+O$_2$ mixture. The flow rate of oxygen ϕ_1, at which p$_{O2}$ starts to increase with increasing ϕ_{O2}, decreases with increasing partial pressure of hydrogen p$_{H2}$ in Ar+O$_2$ mixture.
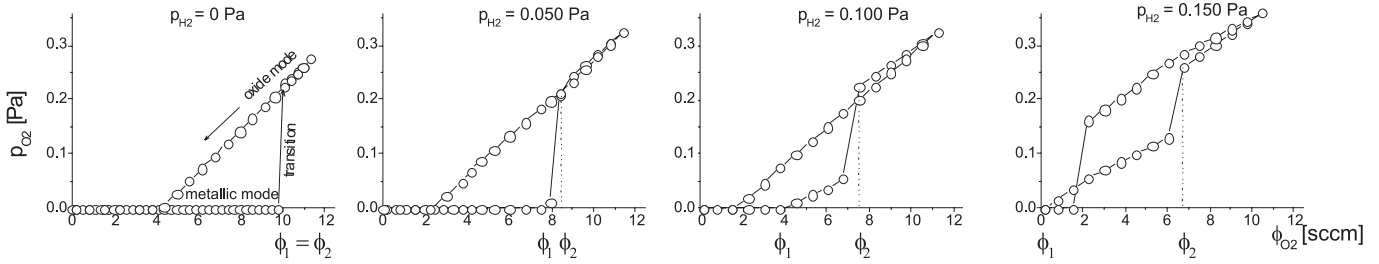
Fig. 1. Effect of addition of hydrogen into Ar+O$_2$ mixture on dependence p$_{O2}$=f(ϕ_{O2}) in reactive sputtering of TiO$_x$ films at I$_d$=3A and p$_T$ = 0.5Pa.

The increase in p$_{O2}$ is due to the incorporation of hydrogen into the target surface and the conversion of pure Ti into a titanium hydride. This conversion results in (1) the decrease of sputtering yield (less Ti atoms is sputtered, less oxygen is gettered and thus p$_{O2}$ increases) and (2) the formation of electrically conductive TiO$_{2-x}$ compound on the target surface due to the substitution of O by H in electrically insulating stoichiometric TiO$_{x=2}$ oxide, formed on target surface. The last fact is of the key importance in sputtering in the oxide mode when the whole target surface is covered by an oxide. Due to the formation of *substoichiometric TiO$_{x<2}$ oxide* the target surface remains *electrically conductive* and arcing on the sputtered target is avoided.

The metallic mode passes into the transition mode at $\phi=\phi_2$. The value of ϕ_2 is lower in the discharge containing hydrogen and decreases with increasing p$_{H2}$. Also, a hysteresis loop is smaller in the sputtering discharge containing the hydrogen, see Fig.1. More details are given in the reference [7].

3.2. Crystallinity and phase composition of TiO$_{x\approx2}$ films

The crystallinity and phase composition of TiO$_{x\approx2}$ films are key parameters deciding on their functional properties [8-10]. Both parameters strongly depend on the partial pressure of oxygen p$_{O2}$, the film thickness h, total pressure p$_T$ and substrate surface temperature T$_{surf}$, see Figs. 2-4. All films were sputtered in the oxide mode.

The crystallinity of TiO$_{x\approx2}$ film is characterized by X-ray diffraction. The narrower is the reflection peak and higher its amplitude the better is the crystallinity of film. The XRD patterns displayed in Figs. 2-4 show that the TiO$_{x\approx2}$ film crystallinity improves with increasing (i) p$_{O2}$, (ii) ratio p$_{O2}$/p$_T$, i.e. with decreasing p$_T$, (iii) film thickness h and (iv) p$_{H2}$. The improvement of the film crystallinity with increasing h clearly indicates that the key role in the TiO$_{x\approx2}$ film crystallization plays the total energy E$_T$ delivered to it during its growth. For more details see the reference [11].
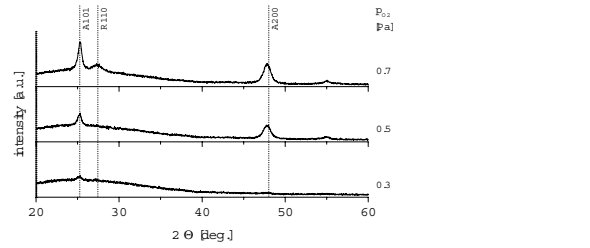

Fig.2. Evolution of XRD patterns of ~1000 nm thick TiO$_2$ films, sputtered in Ar+O$_2$ mixture at U$_d$=520 V and p$_T$=0.9 Pa, d$_{s-t}$=100 mm and a$_D$≈10 nm/min and T$_{surf}$=185°C with increasing p$_{O2}$.
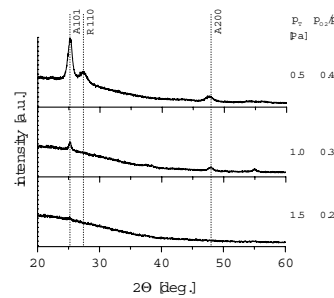

Fig.3. Evolution of XRD patterns of ~1000 nm thick TiO$_2$ films reactively sputtered in Ar+O$_2$ mixture at p$_{O2}$≈const with increasing (i) p$_T$ and (ii) p$_{O2}$/p$_T$.
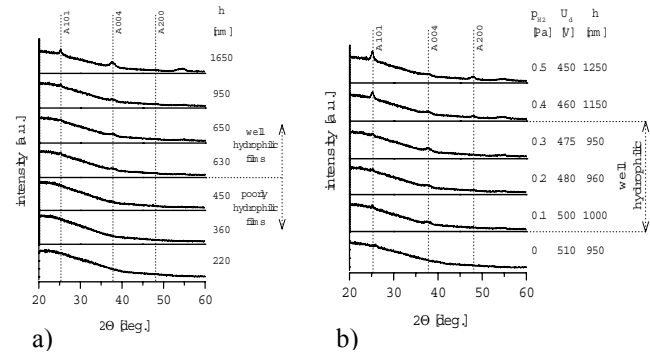

a)   b)

Fig.4. Evolution of XRD patterns of TiO$_{x\approx2}$ films sputtered at I$_d$ = 3A, p$_{O2}$ = 0.3Pa, p$_T$ = 1.5Pa, a$_D$ = 10nm/min, U$_S$=U$_{fl}$ and T$_{surf}$=190°C in Ar+O$_2$+H$_2$ mixture with (a) increasing film thickness h at p$_{H2}$=0.2 Pa and with (b) increasing p$_{H2}$.

The phase composition also strongly depends on the energy E_T delivered to the film. The dominant phase in our crystalline $TiO_{x\approx2}$ films is anatase. As it is shown below the anatase phase is required in the case when the $TiO_{x\approx2}$ film has to exhibit UV induced hydrophilicity.

3.2.1. Effect of hydrogen on film crystallinity

The addition of H_2 into $Ar+O_2$ sputtering gas mixture strongly improves the crystallinity of $TiO_{x\approx2}$ films, see Fig.5. This figure clearly shows that the crystallinity of the $TiO_{x\approx2}$ film improves with increasing p_{H2}.

Also, it is worthwhile to note that the combined effect of increasing p_{H2} and p_{O2} results in a better crystallinity of $TiO_{x\approx2}$ films.

Table 1. Optical transparency T and optical band gap E_g of $TiO_{x\approx2}$ film with different structure.

Film	p_{O2} [Pa]	p_{H2} [Pa]	p_T [Pa]	h [nm]	E_g [eV]	T %	XRD structure in
a-	0.3	0.2	1.5	220	3.32	77.8	Fig. 4a
a-	0.3	0	1.5	510	3.28	77.3	Fig. 4b
fnc-	0.3	0.2	1.5	960	3.28	79.4	Fig. 4b
nc-	0.3	0.5	1.5	1250	3.23	77.7	Fig. 4b
c-	0.2	0	0.5	570	3.08	68.2	Fig. 3

a-, fnc-, nc- and c- denotes the amorphous, fine nanocrystalline, nanocrystalline and crystalline phase, respectively.
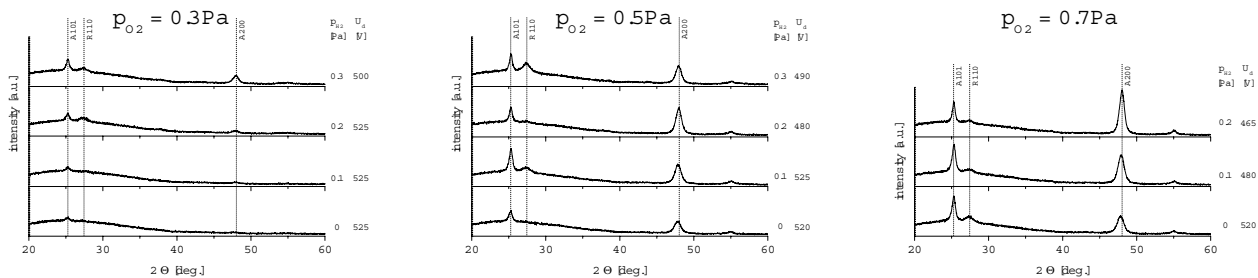

Fig.5. Effect of hydrogen on crystallinity of $TiO_{x\approx2}$ films reactively sputtered in oxide mode at p_T=0.9 Pa and three values of p_{O2}=0.3, 0.5 and 0.7 Pa.

3.3. Optical properties of $TiO_{x\approx2}$ films sputtered in presence of hydrogen

Basic optical properties of the $TiO_{x\approx2}$ film is its transparency T at λ=550 nm and optical band gap E_g. Both parameters depend on the film crystallinity. This means that hydrogen influences T and E_g of the $TiO_{x\approx2}$ film through its structure.

Experimental results show that the fine nanocrystalline $TiO_{x\approx2}$ film films exhibit the highest optical transparency T=79.4%, see Table 1. On the contrary, both the amorphous and crystalline $TiO_{x\approx2}$ films exhibit lower values of T. The crystalline $TiO_{x\approx2}$ film exhibits the lowest transparency T=68.2%.

The optical band gap E_g exhibits a different behavior. The highest value of E_g= 3.32 exhibits the amorphous 220 nm thick $TiO_{x\approx2}$ film. However, the value of E_g of the amorphous $TiO_{x\approx2}$ film decreases with its increasing thickness h, see Table1. The value of E_g strongly depends on the film crystallinity. The value of E_g continuously decreases with improvement of the film crystallinity.

3.3. Hydrophilicity of $TiO_{x\approx2}$ films

The hydrophilicity of $TiO_{x\approx2}$ films induced by the UV light also strongly depends on the film structure. Obtained results are summarized in Table 2. From this table it is clearly seen that fine nanocrystalline (fnc-) $TiO_{x\approx2}$ films exhibit the best hydrophilicity with anatase structure and WDCA $\alpha_{ir}<10°$. These films exhibit a rapid decrease of α_{ir} with increasing time of UV irradiation; $\alpha_{ir}<10°$ is achieved already after ~30 minutes of UV irradiation. These results are in agreement with those obtained for $TiO_{x\approx2}$ films sputtered in the $Ar+O_2$ mixture.

Also, it is worthwhile to note that the fnc- $TiO_{x\approx2}$ films are composed of small A(004) anatase grains immersed in amorphous TiO_2 matrix. The hydrophilicity of $TiO_{x\approx2}$ film improves with increasing intensity of A(004) reflection. Unfortunately, the intensity A(004) starts to decreases when p_{H2} increases above 0.3 Pa. This indicates that p_{H2} used in sputtering of well hydrophilic $TiO_{x\approx2}$ films needs to be optimized.

Table 2. Water droplet contact angle (WDCA) α_{ir} on the surface of ~1000 nm thick amorphous, nanocrystalline and crystalline $TiO_{x\approx2}$ films, produced at I_d=3 A, p_{O2}=0.3 Pa (oxide mode) and p_T=1.5 Pa in presence of hydrogen, i.e. in $Ar+O_2+H_2$ sputtering gas mixture with different structure without and after irradiation by UV light for 20, 40, 60 and 300 minutes. The structure of $TiO_{x\approx2}$ films given in this table are displayed in Fig. 4b.

Film	p_{H2} [Pa]	A101	A004	A200	α_{ir} after UV irradiation for				
					0	20	40	60	300 min
a-	0	-	-	-	60	20	14	12	8
fnc-	0.1	-	yes	-	74	13	10	9	8
fnc-	0.2	-	yes	-	79	12	11	9	8
fnc-	0.3	-	yes	-	77	13	9	9	7
nc-	0.4	yes↑	yes↓	yes	60	27	19	10	9
sc-	0.5	yes↑	yes↓	yes↑	66	28	15	15	11

a-, fnc-, nc-, sc- is the amorphous, fine nanocrystalline, nanocrystalline and slightly nanocrystalline The arrows show increase (↑) or decrease (↓).

4. Conclusions

The experiments describe above show that the addition of H_2 into the $Ar+O_2$ sputtering gas mixture results in

1. The strong change of the p_{O2} vs. ϕ_{O2} dependence.
2. The removal of arcing in DC reactive sputtering of TiO_2 films in spite of the fact that titanium dioxide is electrically insulating.
3. The improvement of crystallinity of TiO_2 films.

TiO_2 films with (i) well crystalline anatase phase and (ii) nanocrystalline structure characterized with broad low intensity anatase peaks can be easily produced. The crystallinity of TiO_2 films produced in presence of hydrogen improves with increasing partial pressure of oxygen, i.e. in the same way, as was already found when TiO_2 films were sputtered in absence of hydrogen, i.e. in the $Ar+O_2$ mixture. Fine nanocrystalline TiO_2 films with anatase nanostructure exhibit the best hydrophilicity with WDCA $\alpha \leq 10°$.

In summary, it can be concluded that the addition of hydrogen in $Ar+O_2+H_2$ sputtering gas mixture makes it possible to produce well hydrophilic TiO_2 films using dc reactive magnetron sputtering. The addition of hydrogen in the $Ar+O_2+H_2$ sputtering gas enables to avoid the arcing on sputtered cathode and thereby to avoid to use the expensive pulse sputtering process in the production of $TiO_{x\approx2}$ films.

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