Porosity Evaluation of TiO₂ Thin Films Deposited Using Pulsed DC-magnetron Sputtering

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Titanium oxide (TiO₂) thin films (1 μm − 4 μm thickness) were deposited on porous Hastelloy-X substrates using pulse dc-magnetron sputtering. The optimal discharge power (400 W), distance between magnetron Ti cathode and substrate (3 cm) were estimated experimentally. When the discharge power, distance between magnetron and substrate was kept constant (optimal), other technological parameters such as bias voltage and oxygen partial pressure were changed to produce higher density films. The optical, structural properties, densification process and porosity of titanium oxide (TiO₂) thin films were investigated. The crystal phase, crystallite size and micro stresses of formed TiO₂ thin films were estimated from XRD measurements. The surface microstructure and the cross section were investigated with SEM. The optical properties were analyzed with ellipsometer (632.8 nm) and the porosity was estimated from the varied values of refractive index. The results show that refractive index changes slightly (from 2.84 to 2.75) with increase of the oxygen partial pressure from 1.3 Pa to 5.9 Pa and formed TiO₂ thin films start to be denser. The growth rate of thin films decreases nearly 15 % with adding the bias voltage to the substrate during the deposition. The refractive index changes from 2.80 to 2.51 with increase of bias voltage from 0 V to –150 V, and the deposited thin films start to be denser, also. Experimental results showed that formation of pure titanium oxide thin films were observed in all experimental cases. Only crystallite sizes and orientation were changed.

Keywords: pulsed dc-magnetron sputtering, TiO₂ thin films, titanium oxide, optical constants, bias voltage, porosity.

1. INTRODUCTION

Titanium dioxide (TiO₂) is one of the extensively studied metal oxides latterly. Titanium oxide thin films have unique dielectric and optical properties [1]. The TiO₂ is one of the most promising candidates for the production of solar-hydrogen as photoelectrode for a photoelectrochemical cell [2]. Also, TiO₂ found to exhibit interesting properties recently, which make it a promising material for chemical gas sensors [3, 4], for antifogging mirror and glass coatings [5], for antiseptic paints and coatings [5]. These films present good durability, high chemical stability, mechanical strength and a high refractive index [2], thus this material is suitable for applications such as antireflection coating [6], multilayer optical coatings [7], optical wave-guides [8] and hydrogen separation and isolation membranes [9].

Many processing techniques such as sol-gel process [10], chemical vapor deposition [11], physical vapor deposition [12] have been used to deposit TiO₂ thin films. Initial data indicates that the method of nano-crystalline (metal oxide) formation can greatly affect the nano-structure and overall performance properties of TiO₂ subject to use range. Technical requirements for TiO₂ thin films and the processes of their formation are very different depending on the specific area of application. The quality of such thin films depends on structural peculiarities, which are influenced by the technological parameters of formation methods. Such parameters are different for each method, however, the same characteristics also depend on certain factors inherent in all

methods. To get the notably dense TiO₂ thin film on the porous substrate is one of significant and actual problem in the technologies for power generation and hydrogen production [13]. To produce dense TiO₂ films of high quality on the porous substrate, first of all it is necessary to investigate the process of such films formation. After analyses of such processes, specific parameters could be chosen. The method for formation of thin films could be simplified and optimal ways of dense TiO₂ thin films formation could be found without losing the required qualities [13]. Magnetron sputtering is one of the most perspective, but the process is complicated and has not been analysed comprehensively. Therefore, the purpose of this paper was to produce dense TiO₂ thin films on porous substrates by pulsed dc-magnetron sputtering changing technological parameters (oxygen partial pressure and bias voltage), to analyze them (XRD, SEM, ellipsometer), and define the impact of the process parameters.

2. EXPERIMENTAL

TiO₂ thin films synthesis was done employing pulse DC magnetron system with cooled by water high purity (99.98 %) Ti target 100 mm in diameter. The temperature of the cooled cathode did not exceed 50 °C and was not influenced by the magnetron discharge power during the experiment. The vacuum chamber has the inlets of argon and oxygen gases. The distance between magnetron and substrate was kept at 3 cm. Some of the experiments were performed with the bias voltage U_B (0 V ÷ −150 V). The TiO₂ thin films were deposited on the porous Hastelloy-X (Ni, Cr, Fe, Mo and Co alloy) substrates. The main experimental parameters are presented in the Table 1. The position between the magnetron cathode and the substrate

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during the deposition of thin films was parallel with a shutter placed between the target and the substrate. The chamber was pumped to background pressure of $3 \cdot 10^{-3}$ Pa before each experiment and filled with high purity (99.999 %) oxygen gas to working pressure 1.3 Pa – 6.0 Pa.

Table 1. Experimental parameters

Experimental parameters	Values
Diameter of Ti cathode, cm	10
Discharge power, W	400
The distance between Ti cathode and substrate, cm	3
Initial pressure, Pa	$3 \cdot 10^{-3}$
Working pressure (O$_2$), Pa	1.3 – 6.0
Substrate	Hastelloy-X

The TiO$_2$ thin films thickness was calculated from the weight change, which was determined weighing substrate before and after deposition. The experimental measurements of the thin film thickness were performed by employing precise (10^{-8} kg) microbalances. The density of TiO$_2$ was taken from catalog (3.9 g/cm^3).

The thin film structure was analyzed by X-ray diffraction (XRD) with the 2Θ angle in the range of $20° – 70°$ using Cu K$_\alpha$ radiation ($\lambda_{Cu} = 0.15405$ nm) in steps of 0.05° (standard Bragg-Brentan geometry). The crystal structure, crystallographic phase, micro strains and average crystallite dimension D of thin films were obtained using WinFit program. The surface and cross – section of samples was investigated by a scanning electron microscope (JSM 5600). The optical properties of deposited TiO$_2$ thin films were investigated using a laser ellipsometer Gaertner L117 with He-Ne laser ($\lambda = 632.8$ nm) and for calculation optical constants (refractive index and extinction coefficient) "FilmEllipse SCI Scientific Computing International" program was used. The porosity of deposited TiO$_2$ thin films was estimated from the varied values of refractive index [14]. The expression for evaluating porosity in terms of the refractive index (~ 600 nm) of the film was:

$$P = 1 - \frac{n^2 - 1}{n_d^2 - 1}, \tag{1}$$

where P is the pore volume fraction, n is the refractive index of the porous film, and n_d is the refractive index of the film after densification [14].

3. RESULTS AND DISCUSSIONS

Thin films of titanium oxide (1 μm ÷ 4 μm) were deposited in O$_2$ atmosphere on porous Hastelloy-X (Ni, Cr, Fe, Mo and Co alloy) substrates at different oxygen pressure and bias voltage. The discharge power (400 W), the distance between the magnetron cathode and the sample $d = 3$ cm was kept constant.

It was found that deposition rate of titanium oxide thin films was dependent on the oxygen partial pressure p_{O2}. The deposition rate slightly increases from 10.1 nm/min. to 11.2 nm/min. increasing oxygen pressure p_{O2} from 1.3 Pa to 2.3 Pa (bias voltage $U_B = 0$ V). The deposition rate starts to decrease and at $p_{O2} = 5.9$ Pa the deposition rate was 9.3 nm/min. by further increasing of oxygen pressure. The

dependence of bias voltage on the growth rate is shown in Fig. 1. Explaining these dependencies one should keep in mind that the magnetron cathode is clean at low oxygen partial pressure. The oxygen atoms incorporate in the growing layer and the growth rate of thin film is increasing. The ionic sputtering rate is higher than oxygen adsorption rate on the target cathode. The magnetron cathode is covered by the oxygen layer increasing p_{O2}. For this reason the sputtering and thin films growth rates decreases.

It is known that bias voltage on the substrate could cause desorption, formation of defects and sputtering. The bias can influence the structural properties of formed titanium oxide thin films because of the additional bombardment of low energy ions during the formation process. This can influence the growth rate and the mechanism of thin film formation. To take count of it, the influence of bias voltage on the formation process of titanium oxide thin films were investigated. The bias voltage was kept negative in all experiments.

The influence of bias voltage (–70 V, –100 V, and –150 V) on the growth rate is shown in Fig. 1. The growth rate decreasing almost 10 % at bias voltages $U_B = -70$ V and –100 V. The growth rate decreases more than 5 % by further increase of bias voltage $U_B = -150$ V (the discharge power was kept constant 400 W and the oxygen pressure was changed from 1.3 Pa to 6.0 Pa). Such growth rate decrease could be explained that the sputtering coefficient of adsorbed atoms, which are in active state, is much higher than for the atoms which are in the stable state. The growing layer is bombarded by low energy ions. Deposition rate reduction caused by bias could be explained by additional oxygen ions bombardment, which can initiate sputtering of the growing oxide film.
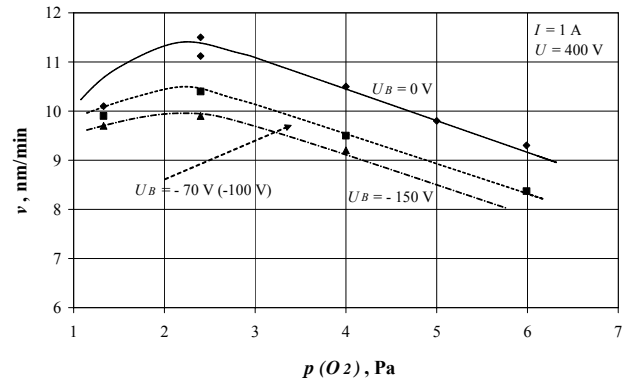
Fig. 1. Deposition rate as a function of oxygen pressure and bias, when discharge current ($I = 1$ A), discharge voltage ($U = 400$ V) and distance between cathode and substrate ($d = 3$ cm) were fixed

TiO$_2$ thin films deposited at various bias voltages were examined by XRD. XRD spectra revealed crystalline nature of titanium oxide films (Fig. 2). From Fig. 2 it was clearly identified, that thin titanium oxide films were with the preferred (101) crystalline orientation. Highly textured films with the preferred crystalline orientation (200) were observed with the bias $U_B = -100$ V. Intensities of peaks (004) and (112) became bigger with the higher bias. The peaks (105) and (211) disappeared at the bias $U_B = -150$ V.

The peak (100) inherent to rutile phase with the bias $U_B = -150$ V. The anatase phase was formed in all other cases. The crystallographic orientation, crystallite size and micro stress values of the formed TiO_2 thin films are presented in Table 2. The crystallite size decreases by increasing the bias. It can be caused by the bombardment of low energy oxygen ions.
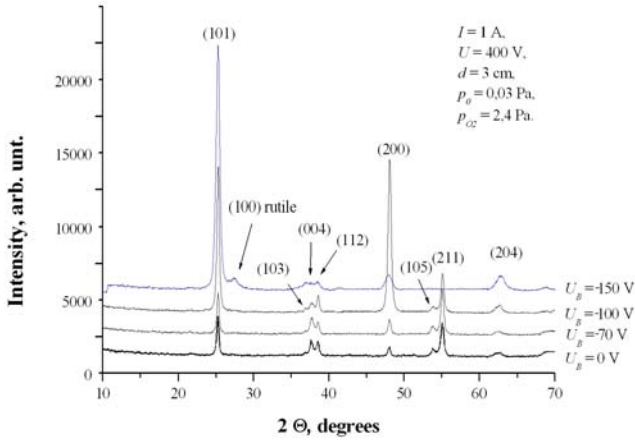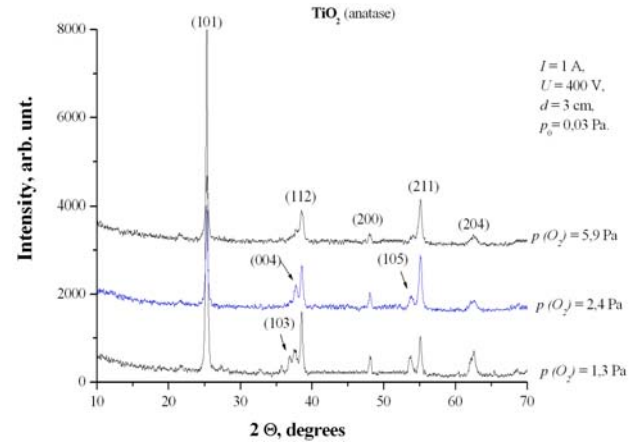

Fig. 2. X-ray diffraction patterns of TiO_2 thin films deposited on the Hastelloy-X substrates as a function of applied bias ($U_B = 0$ V, $U_B = -70$ V, $U_B = -100$ V, $U_B = -150$ V)

Table 2. The influence of the bias voltage on the structure of deposited TiO_2 thin films (A – anatase phase, R – rutile phase, e – stress)

Θ, °	(hkl)	D (nm)			e (%)		
		−70 (V)	−100 (V)	−150 (V)	−70 (V)	−100 (V)	−150 (V)
25.25	A (101)	52.9	23.0	16.7	0.00	0.53	0.15
27.46	R (100)	–	–	10.1	–	–	0.90
37.60	A (004)	29.5	9.1	–	0.25	0.66	–
38.62	A (112)	52.7	52.4	7.0	0.14	0.05	0.75
48.11	A (200)	26.6	26.4	11.8	0.21	0.19	0.05
53.80	A (105)	15.3	7.7	–	0.24	0.42	–
55.03	A (211)	41.9	21.9	–	0.00	0.27	–
62.68	A (204)	12.6	5.5	6.0	0.22	0.52	0.67

X-ray diffraction patterns of TiO_2 thin films deposited on the Hastelloy-X substrates as a function of oxygen pressure ($p_{O2} = 1.3$ Pa, $p_{O2} = 2.4$ Pa, $p_{O2} = 5.9$ Pa) are shown in the Fig. 3. The discharge current, discharge voltage and the distance between cathode and substrate was kept constant ($I = 1$ A, $U = 400$ V and $d = 3$ cm). All peaks are in good agreement with the TiO_2 standard anatase phase peaks. From Fig. 3 it was clearly identified, that thin titanium oxide films were with preferred (101) crystalline orientation. Intensities of peak (101) became smaller with the higher oxygen pressure. Intensities of peaks (105) and (004) became smaller and at $p_{O2} = 5.9$ Pa the peaks disappeared. It could be seen the peak (103)

preferred crystalline orientation at the pressure $p_{O2} = 1.3$ Pa. The crystallographic orientation, crystallite size and micro stress values of formed TiO_2 thin films are presented in Table 3. The crystallite size is increasing by decreasing the oxygen pressure.

Fig. 3. XRD patterns of TiO_2 thin films deposited on the Hastelloy-X substrates as a function of oxygen pressure ($p_{O2} = 1.3$ Pa, $p_{O2} = 2.4$ Pa, $p_{O2} = 5.9$ Pa)

Table 3. The influence of the oxygen pressure on the structure of deposited TiO_2 thin films (A – anatese phase, e – stress)

Θ, °	(hkl)	D (nm)			e (%)		
		1.3 (Pa)	2.4 (Pa)	5.9 (Pa)	1.3 (Pa)	2.4 (Pa)	5.9 (Pa)
25.25	A (101)	55.2	46.2	39.5	0.40	0.01	0.00
36.95	A (103)	53.8	–	–	0.24	–	–
37.60	A (004)	44.9	29.9	–	0.02	0.12	–
38.62	A (112)	116.0	40.6	18.8	0.01	0.12	0.25
48.11	A (200)	27.9	26.9	13.3	0.02	0.09	0.76
53.80	A (105)	19.8	17.2	–	0.08	0.17	–
55.03	A (211)	35.3	16.7	14.6	0.03	0.09	0.24
62.68	A (204)	20.2	7.1	6.2	0.07	0.51	0.33

The influence of the oxygen pressure and the bias voltage on the optical constants (n – refractive index, k – extinction coefficient) of deposited TiO_2 thin films is presented in Table 4.

The ellipsometric measurements ($\lambda = 632.8$ nm) show that increasing of the bias voltage determinates that the refractive index decreases and extinction coefficient increases of the formed titanium oxide thin films. The refractive index is 2.8 at bias $U_B = 0$ V ($I = 1$ A, $U = 400$ V, $p_{O2} = 2.4$ Pa) and it decreases till 2.51 at bias $U_B = -150$ V. The refractive index and extinction coefficient decreases slightly (n from 2.84 to 2.75, and k from 0.008 to 0.001) increasing the partial pressure of oxygen from 1.3 Pa till 5.9 Pa.

Ming Zhang at al. [17] reported that the refractive index depends on the bias voltage. The results of these authors show that the refractive index of the TiO_2 deposited by pulsed bias arc ion plating becomes lower at higher bias voltage. The value of n of the film deposited at 0 V is higher ($n = 1.5$) than that of the film at –100 V ($n = 1.4$). The values of the refractive index in our work are higher.

Table 4. The influence of the oxygen pressure and the bias voltage on the optical constants of deposited TiO_2 thin films (n – refractive index, k – extinction coefficient)

| U_B ($p_{O2} = 2.4$ Pa)	0 V	–70 V	–100 V	–150 V
n	2.80	2.70	2.62	2.51
k	0.001	0.001	0.002	0.004
p_{O2} ($U_B = 0$ V)	1.3 Pa	2.4 Pa	5.9 Pa	
n	2.84	2.80	2.75	
k	0.008	0.002	0.001	

The crystal structure of the formed thin films is influenced by the substrate temperature and film growth rate. The microstructure of thin films can be roughly predicted using the Movchan and Demchishin or the Thorthon structure diagrams [15, 16]. The microstructure could be predicted to keep in mention the processing temperature normalized to the melting point of the coating material (T / T_m) and the process pressure. In our case, deposited TiO_2 thin films microstructure corresponds to the Zone 1 (columnar growth) where the processing temperature normalized to the melting point of the coating material (T / T_m) is lower than 0.3.

The SEM images of the cross sections of TiO_2 thin films deposited on Hastelloy-X substrates are presented in Fig. 4 and Fig.5.

In all oxygen pressures and bias voltages the microstructure of formed films is columnar. The morphology of the surface region of thin films has a crystalline columnar texture with all columnar grains oriented in the same direction, namely perpendicular to the substrate, and with a predominantly open micro porosity. The microstructure consists of parallel columns with gaps in between. The width of columns increases with the increase of the bias voltage U_B (Fig. 4). Additional bombardment by ions changes the temperature of substrates ($U_B = 0$ V – the temperature T does not exceed 100 °C, $U_B = -150$ V – T increases to 400 °C) and that influence the width of columns. A more compact and dense structure is observed as the substrate bias is applied (Fig. 4). It can be related to the activation processes initiated by additional ion bombardment induced by applied bias to the substrate. The cross section of samples prepared at different pressure (p_{O2} = 1.3, 2.4, and 5.9 Pa) are present in Fig. 5. Increasing the partial oxygen pressure the columns width starts to be narrower (Fig. 5).

Thin films with the denser structure were formed at lower pressure. In this case ions arriving to the substrate at lower pressure have higher energy and bombardment by energetic ions leads to the increase of surface energy and formation of denser structures. The surface SEM images of
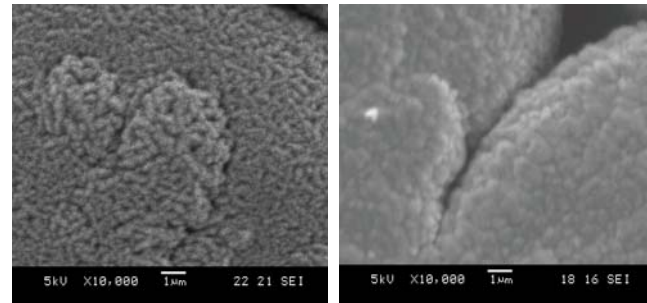
titanium oxide thin films formed with different bias voltage ($U_B = 0$ V, and $U_B = -150$ V, when $I = 1$ A, $U = 400$ V, $d = 3$ cm, $p_{O2} = 2.4$ Pa) confirm these facts (Fig. 6).
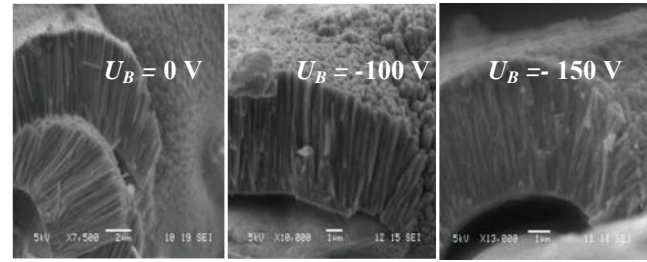
Fig. 4. SEM images of cross sections of titanium oxide thin films formed with different bias voltage ($U_B = 0$ V, $U_B = -100$ V and $U_B = -150$ V, when $I = 1$ A, $U = 400$ V, $d = 3$ cm, $p_{O2} = 2.4$ Pa)
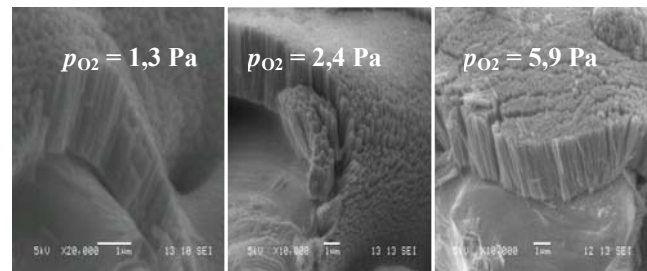
Fig. 5. SEM images of cross sections of titanium oxide thin films formed with different oxygen pressures ($p_{O2} = 1.3$ Pa, $p_{O2} = 2.4$ Pa and $p_{O2} = 5.9$ Pa, when $I = 1$ A, $U = 400$ V, $d = 3$ cm, $U_B = 0$ V)

Fig. 6. Surface SEM images of titanium oxide thin films formed with different bias voltage ($U_B = 0$ V, and $U_B = -150$ V, when $I = 1$ A, $U = 400$ V, $d = 3$ cm, $p_{O2} = 2.4$ Pa)

Table 5. The influence of the oxygen pressure and the bias voltage on the porosity of deposited TiO_2 thin films

Bias voltage, V	Reduction of porosity, %
0	0
–70	5.88
–100	11.11
–150	19.21
Oxygen pressure, Pa	
1.33	0
2.40	2.22
5.90	5.14

The influence of the oxygen pressure and the bias voltage on the porosity of deposited TiO_2 thin films is presented in the Table 5. The porosity was calculated according [14] from the refractive index measurements (Table 4). The initiate refractive index value was taken of TiO_2 thin films formed at $p_{O2} = 1.3$ Pa and $U_B = 0$ V. It could be seen that by adding bias voltage $U_B = -70$ V the porosity decreases ~6 %, and at $U_B = -150$ V the porosity decreases ~20 % (Fig. 7). Also, it could be seen the reduction of the porosity by increasing the oxygen pressure, when the initial porosity was took 100 % ($U_B = 0$ V, $p_{O2} = 1.3$ Pa).
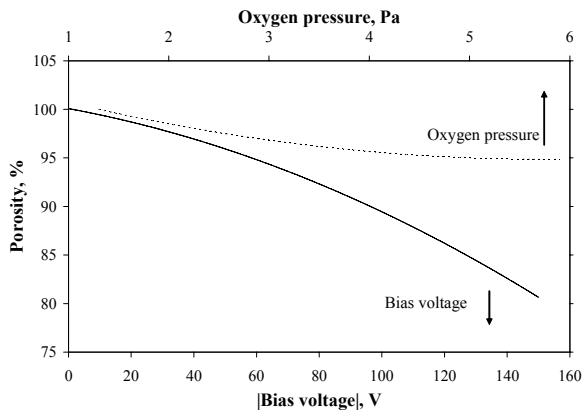
Fig. 7. The influence of the oxygen pressure and the bias voltage on the porosity of deposited TiO_2 thin films

4. CONCLUSIONS

Thin films of titanium oxide (1 μm ÷ 4 μm) were successfully deposited on the porous Hastelloy-X substrates. According to the obtained results it could be seen that the titanium oxide thin films growth rate on porous substrates depends on oxygen pressure and bias voltage. The pressure influence on deposition rate is non linear. The decrease of thin films thickness with the increase of oxygen pressure can be explained by formation of oxide layer on the top of magnetron target and decrease of target sputtering yield. The deposition rate decreases ~15 % by adding bias –150 V, also. The oxygen pressure p_{O2} does not influence crystal phase of formed TiO_2 thin films. The formed films have anatase phase with preferred (101) crystalline orientation. The refraction index decreases from 2.84 to 2.75 with growing up of the oxygen pressure from 1.3 Pa to 5.9 Pa. The deposition rate decreases with the increase of bias voltage. Moreover the appliance of bias induces forming of rutile phase titanium oxide with the increased density and decrease of refraction index form 2.80 to 2.51. The bias effects were close related to initiation of additional substrate bombardment by oxygen ions, which can cause densification or sputtering of the growing films. Thin films with denser microstructure were formed at high bias voltage (–150 V) and lower deposition pressure (1.3 Pa).

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