Titanium oxide thin films deposited by high-power impulse magnetron sputtering

S. Konstantinidis [a],*, J.P. Dauchot [a], M. Hecq [b]

[a] Unité de Chimie Inorganique et Analytique, Materia Nova, Avenue Copernic 1, 7000 Mons, Belgique, Belgium
[b] Laboratoire de Chimie Inorganique et Analytique, Université de Mons-Hainaut, bâtiment Materia Nova, Avenue Copernic 1, 7000 Mons, Belgique, Belgium

Abstract

Ionized physical vapor deposition processes are of great interest for surface modification because the flexibility of the thin film deposition process can be increased by ionizing the metallic vapor. Recently, high-power impulse magnetron discharges have been implemented to achieve high ionization rates.

Thin films of titanium oxide have been deposited on glass and steel substrates using 450×150 mm rectangular titanium target in argon–oxygen atmosphere. The average power delivered to the plasma is ranging between 1.5 and 2 kW and peak current and voltage are respectively 200 A and 900 V.

Films are characterized using Scanning Electron Microscopy, Grazing Incidence X-ray Diffraction and Optical Transmission Spectroscopy. One of the major findings is the presence of rutile deposited on steel substrate (even for 0 V bias grounded substrate) and the significant increase of the refractive index of the films deposited on glass compared to thin films deposited via conventional direct current bipolar pulsed magnetron sputtering. Films synthesized by high-power impulse magnetron sputtering are denser.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Ionized physical vapor deposition; Phase transitions; Titanium oxide; X-ray diffraction

1. Introduction

Titanium oxide presents many interesting properties in various fields (optics, electronics, iron and steel…). Among the most remarkable, one can mention that titanium oxide is transparent in the visible range of the electromagnetic spectrum, has semiconducting properties and presents several crystalline phases, in particular anatase and rutile. According to the literature, when it has the anatase structure, the film shows photocatalytic properties used, for example, to destroy polluting organic substances (hydrocarbons, NO_x…)[1]. Rutile is characterized by both refractive index [2] and hardness [3] higher than anatase.

Most of the time, titanium oxide films deposited by conventional magnetron sputtering are amorphous or in the anatase form. In order to promote thin film crystallization, it is necessary to supply energy to the growing film by heating or via particle (ion [4]) bombardment. According to Martin et al. [3]

anatase appears at an annealing temperature of 300 °C, rutile is formed at higher temperature (above 900 °C). For titanium oxide films grown by filtered arc deposition on (100) conducting silicon substrates, rutile is obtained for substrate bias voltage of −100 V and lower [4]. In both cases, following the amount of energy supplied, anatase is the first phase to appear. Rutile needs a larger amount of energy to be synthesized. Obtaining rutile proves the energetic condensation of the film.

For the present study, we have synthesized titanium oxide (TiO_x) thin films on steel and glass substrates using High-Power Impulse Magnetron Sputtering (HIPIMS), an emerging technology that has previously shown enhancement of thin film quality [5–7]. HIPIM allows a strong ionization of the sputtered metallic vapor. Ionization rate is found to be higher than 30% [8,9]. This feature opens new perspectives for thin film deposition because energetic condensation of the film is easily achieved. As deposited species are ions, it is possible to calibrate metal ions energy and trajectory by biasing the substrate.

TiO_x coatings are also deposited by conventional Direct-Current Bipolar Pulsed Magnetron Sputtering (DCBPMS).

---

* Corresponding author. Tel.: +32 65 37 38 45; fax: +32 65 37 38 41.
E-mail address: stephanos.konstantinidis@umh.ac.be (S. Konstantinidis).

Refractive index, morphology and crystalline structure of the film deposited by HIPIMS and DCBPMS are compared.

2. Experimental details

Titanium oxide films are deposited in a TSD400CD (HEF R&D) semi-industrial vacuum chamber. The rectangular titanium target (450×150 mm) is sputtered in a mixture of argon and oxygen. Mass flows are 105 SCCM (Standard Cubic Centimetre per Minute) and 80 SCCM, respectively. In this condition, the titanium sputtering target is fully poisoned. Working pressure is kept constant at 1 Pa (1×10^{-2} mbar).

The HIPIM power supply [10] is used to increase the titanium vapor ionization rate by applying high-voltage during short duration pulses (7 µs in the present experiments). Discharge voltage and current are measured with appropriate probes, as described in our previous papers [9,11]. Discharge voltage peak value is 900 V, peak current is around 200 A. Average powers applied to the cathode are in the range between 1.5 and 2 kW following the repetition frequency which is respectively set between 2 and 3 kHz.

The DCBPM power supply (ENI RPG50) is used with a 150 kHz repetition frequency and a positive pulse 2 µs in duration. It is known that using such a bipolar pulsed power supply increases the film quality and process stability during reactive sputtering.

Thin films are deposited by both techniques in the same conditions (average power, substrate to sputtering target distance and gas composition) in order to be compared.

Glass substrates are 4 mm thick and cleaned using degreasing detergent (RBS-35, pH>10) prior to deposition. Steel foils are 0.2 mm thick and also cleaned with the degreasing solution. Substrates are grounded, floating or biased during the coating process. Bias is supplied in form of pulsed bipolar waves by an ENI RPG50 power generator. Bias parameters are always 250 kHz frequency with 0.5 µs of reverse voltage duration. Substrates are set approximately 7 cm from the target surface.

In order to obtain pictures showing film morphology, Scanning Electron Microscopy (SEM) observations are carried out with a Phillips XL20 microscope. Coated glass substrates are analyzed using a Varian Cary 5G UV–visible–near infrared transmission spectrometer. Via transmission spectra and film thickness it is possible to estimate the refractive index of coated material. Film thickness is measured thanks to a mechanical profilometer (DEKTAK 3030). Finally, crystalline structure is obtained by Grazing incidence X-ray Diffraction (GXRD) measurements in a Siemens D5000 diffractometer.

3. Results and discussion

3.1. Coating thickness and morphology

Titanium oxide film thickness was measured first. In the present study, films are simultaneously deposited on glass and steel substrates in the following synthesis conditions: substrate bias of −50 V and 6 h duration, it is found that films deposited by HIPIMS are thinner than those produced by DCBPM sputtering.

On glass substrate, the thickness of film deposited by HIPIMS is 660 nm while 1350 nm for the film synthesized by DCBPMS. We presume the trend would be the same for films grown on steel. It was not possible to directly measure film thickness with the profilometer because of the steel substrate surface roughness. Eventually, thickness disparities could increase for steel because being such a conductive substrate, the bias should be equally or more efficient than on glass.

Three causes can explain this behaviour in thickness disparities: first, a lowered deposition rate with HIPIM sputtering. Secondly, the densification and/or the re-sputtering of the films by the ions produced during the HIPIM discharge. Third, DCBPM generators are optimized to run in the poisoned mode. It has been previously demonstrated that deposition rate is reduced compared to conventional pulsed DC sputtering while using HIPIM generator at the same working power [6,9]. Sproul et al. [6] report a deposition rate ratio (HIPIM over pulsed DCM discharge) of
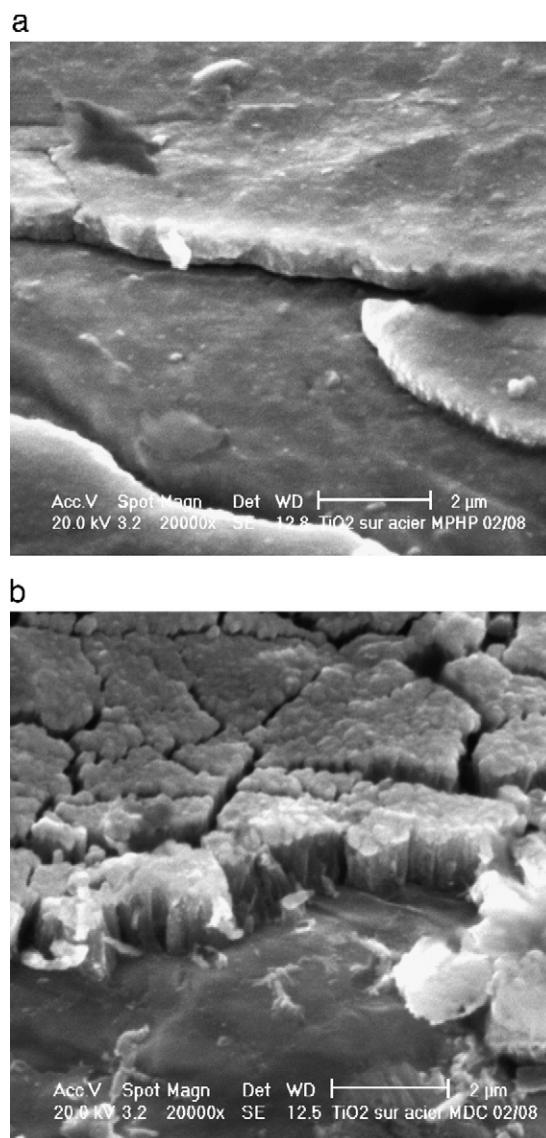
Fig. 1. (a) SEM picture of film synthesized by HIPIMS on steel substrate with a −50 V bias. (b) SEM picture of film synthesized by DCBPMS on steel substrate with a −50 V bias.
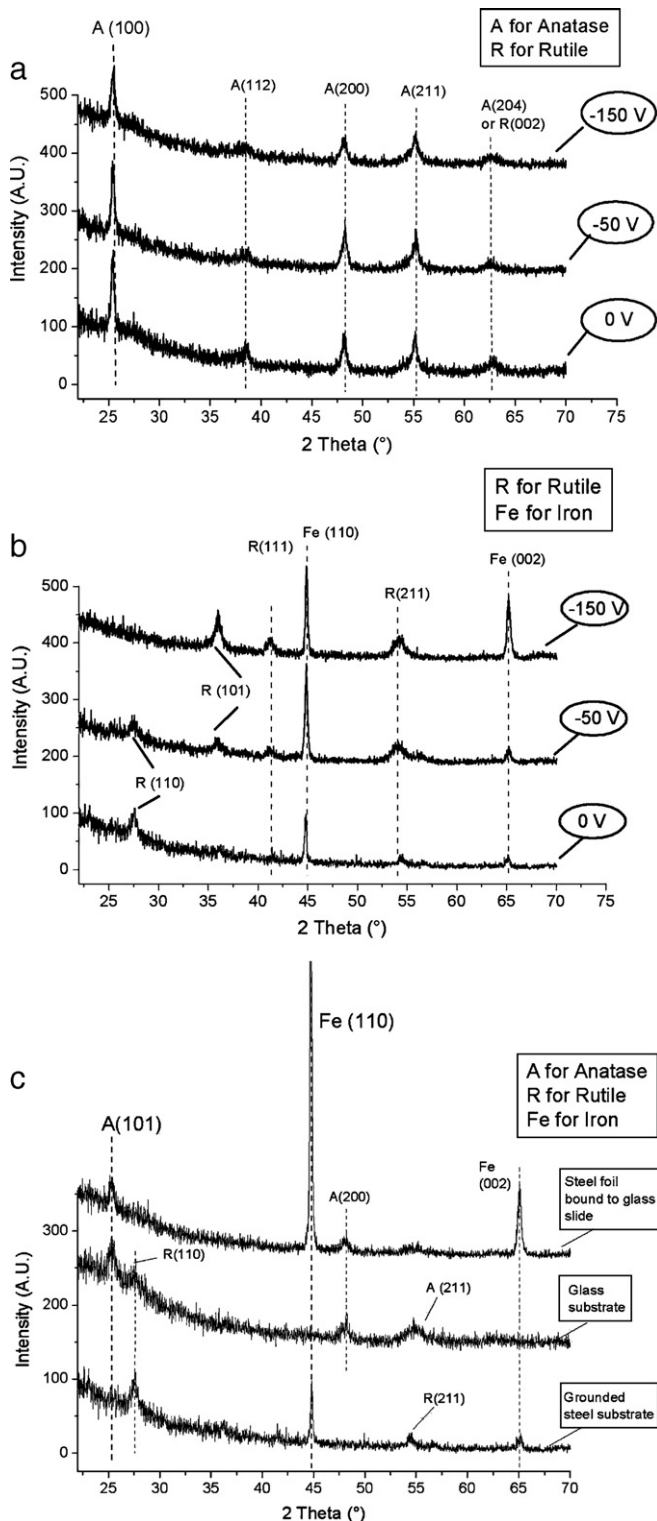
Fig. 2. (a) Diffraction diagrams obtained for TiO$_x$ coatings deposited on glass by HIPIM sputtering technique, at three different bias voltages. (b) Diffraction diagrams obtained for TiO$_x$ coatings deposited on steel by HIPIM sputtering technique, at three different bias voltages. (c) HIPIMS deposited films. Effect of setting the steel substrate to the floating potential (bound to a glass slide) on the diffraction peaks. Anatase is found, as for glass coated substrate, instead of rutile.

approximately 30% in the case of aluminium oxide deposition. With the electric generator used in our HIPIMS experiments, we are using short pulses (duration <20 μs). Using short pulses is key

to minimizing the deposition rate reduction [9]. Furthermore, when DC bipolar pulse magnetron sputtering generator is carefully tuned, it is possible to increase the deposition rate [12,13]. Be that as it may, deposition rate in HIPIMS should be inferior to bipolar pulsed sputtering.

For glass substrates, morphology does not present significant dissimilarities between HIPIM and DCBPM sputtered films. Both films look columnar. Thickness difference between both deposition methods should therefore be principally attributed to lowering of deposition rate, as thickness is measured on glass.

As it can be seen in Fig. 1a, films look denser when they are deposited on biased (−50 V, DCBP bias) steel foils. Microscope observations are taken where the film has cracked due to substrate cutting in order to observe the film side. On these pictures (Fig. 1a and b), one can see the influence of working with HIPIM (Fig. 1a). Films exhibit dense packing while they are found to be of columnar structure in the case of DCBPM (Fig. 1b).

3.2. Crystalline structure

Crystal structure is determined by GXRD measurements. All deposition processes are done during 150 min, within the same deposition conditions (pressure and gas mixture, average power and substrate position).

Films deposited on glass by HIPIMS present an anatase crystalline structure whatever the bias may be (Fig. 2a). Bias amplitude has only a small effect on diffraction peak intensities. Diffraction diagrams obtained for TiO$_x$ on steel as synthesized with HIPIMS for three bias voltages are reproduced in Fig. 2b. One can note that, besides the peaks corresponding to steel, only rutile peaks are present on the diffraction spectrum. Increasing the bias voltage produces a texture modification of the film. (110) Peak disappears and (111) and (101) peaks gain in intensity. Film sputtering (and the subsequent reduced film thickness) or the strong coating densification should be responsible for the increased iron peak intensities as bias voltage is amplified.

To explain the presence of anatase on glass, one first think of the large amount of metallic ions and electrons produced during the pulse in HIPIMS. Electrons are the first particles to reach the substrate. It has been previously estimated that in such HIPIMS experiments, plasma density is superior to those commonly measured in DCMS discharges [14]. Then the bombardment of the coated substrate (glass or steel) will be more intense for HIPIMS than in the case of DCBPMS. It is known that electron irradiation modifies the physicochemical properties of so treated materials [15,16]. The electron flux can heat the substrate surface and induce morphological and chemical modifications.

The energy deposited on the substrate where the film is growing will be a function of: first, the plasma density and second, the capacitance between the film surface and the ground. As a consequence, for the same plasma density, the energy supplied to the film by the electron and ion bombardment will be more important for a biased or grounded conducting substrate (steel), even if the substrate is coated by an insulating titanium oxide thin film. In the case of a conductive substrate coated by an insulating film, the electric capacitance between the film surface and the conductive substrate is large. Then, the electron current necessary
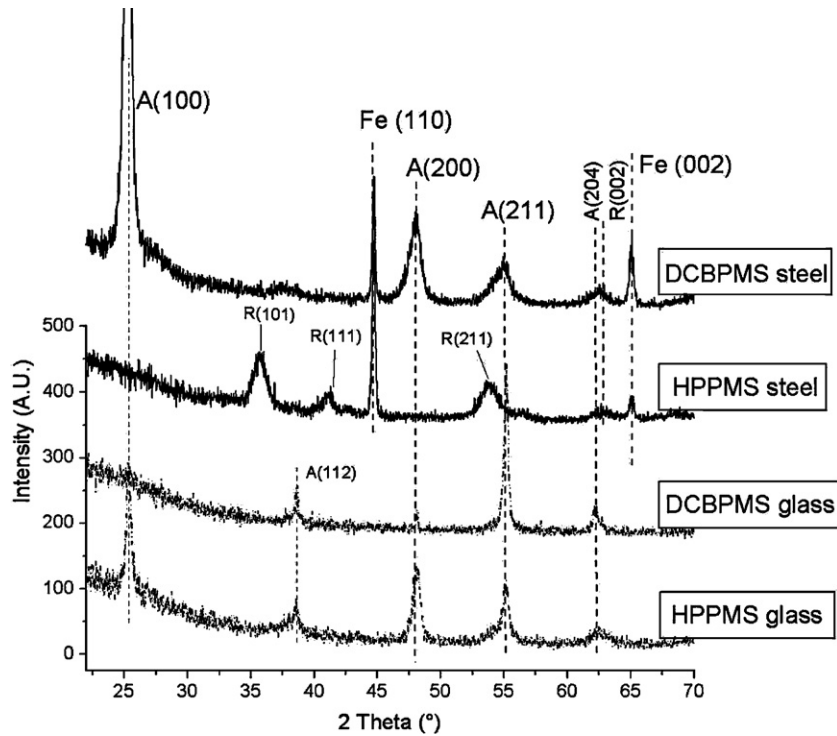
Fig. 3. Comparison of diffraction patterns obtained for steel and glass substrates coated by HIPIMS and DCBPMS techniques, for a −50 V bias voltage.

to bias the substrate must be large. Consequently, the ion bombardment will be intense too and the energy supplied to the film will be high. On steel substrates, the high-temperature crystalline phase of titanium oxide (rutile) is obtained.

In the case of an insulating substrate (glass plate), the electric capacitance between the film surface and the ground is very low compared to steel substrate. The electron flux necessary to bias the surface will be smaller and then, a weaker ion current will also be necessary to compensate the negatively charged substrate surface during the pulse. For the same reason, the bias applied in the form of a DC bipolar pulse has practically no effect.

We can also call to mind that glass is not a good heat conductor. During deposition, the thermocouple placed in the bottom of the vacuum chamber several centimetres behind the substrate holder showed a temperature increase inside the vacuum chamber, up to 90–100 °C at the end of the deposition process. One can imagine that a glass surface would be hotter. This temperature elevation would also increase the probability for TiO_x film crystallization. In these circumstances, only the low-temperature crystalline phase of titanium oxide (anatase) could be obtained.

However, it seems that the physicochemical nature of the substrate does not influence the crystalline structure of the TiO_x film. Films grown in the same conditions as those corresponding to Fig. 2a and b by HIPIMS but on a steel foil glued to a glass substrate present an anatase structure similar to the one obtained on the simultaneously coated glass, as seen on diffractograms in Fig. 2c.

Thus it seems that the substrate electric connection to the ground is an important parameter. In other words, the substrate must allow electrons and ions to intensively bombard the substrate to get the rutile phase. Maybe the outstanding

properties of the films grown by HIPIMS are not only induced by the large ionization rate of the sputtered vapor but also by the intense electron flux generated by the high-voltage pulses that reach the substrate.

In this last section, diffractograms of films deposited by HIPIMS and DCBPMS on glass and steel are presented (see Fig. 3). Syntheses are run with −50 V of bipolar pulsed bias and an average power of 1.8 kW. For steel, while rutile TiO_x films are deposited by HIPIMS, the anatase structure is found with DCBPM. This result emphasizes a more energetic condensation process of the growing film with the HIPIMS technique. When substrate bias is effective, the growing film can take full
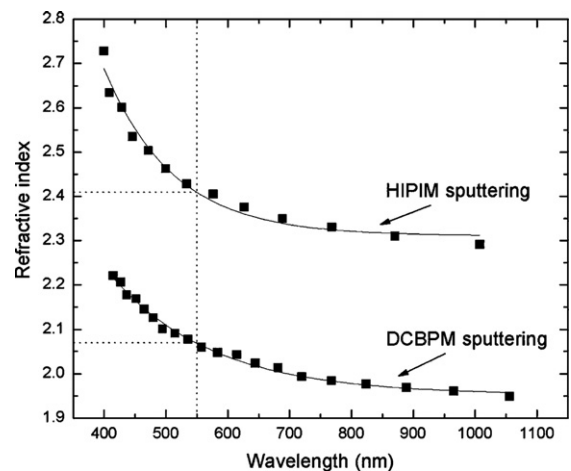

Fig. 4. Refractive index as calculated through optical transmission measurements for titanium oxide films deposited on glass by both HIPIMS and DCBPMS techniques, with −50 V of bias.

advantage of vapor ionization. Ion bombardment is effective; films are denser (Fig. 1a) and present the high-temperature stable crystalline structure of rutile. On glass, both deposition methods lead to anatase formation but textures are different. For HIPIMS, spectrum reveals a multi-oriented structure. Several diffraction peaks are present. For DCBPM, the film is more (211) oriented.

3.3. Refractive index

Refractive index is calculated thanks to the optical transmission spectra, by using minima and maxima of the interference fringes present on optical transmission curves. In Fig. 4, refractive indexes are compared as a function of the wavelength for titanium oxide films deposited by both methods, with a bias of −50 V. Curves corresponding to HIPIM sputtered oxide film is above those representing DCBPM sputtered coatings. At 550 nm, HIPIMS gives a film characterized by a refractive index n of 2.42. For DCBPM sputtering, n equals 2.07. This behaviour and the absolute values of the refractive indexes are consistent with the literature. In Ref. [17], the same increase of the refractive index is presented for TiO_X film deposited on glass: $n \sim 2.45$ at 550 nm with film deposited by HIPIMS while $n \sim 2.1$ for film synthesized by DC sputtering. These authors [17] explain the significantly increased refractive index by the film densification as they do not observe any crystallization. Bendavid et al. [4] report an increased value of the refractive index as they increase the conductive silicon substrate bias voltage from 0 to −400 V using filtered arc. At −400 V, rutile is found and the refractive index is about $n \sim 2.72$. At 0 V bias, when the film has anatase structure, $n \sim 2.62$. In Ref. [18], increase of refractive index is attributed to the grain crystalline orientation in anatase films. As orientation is not scattered, films are denser and the refractive index is augmented. In the present experiments, a higher value of n is found for film deposited by HIPIMS which presents random orientation corresponding to anatase while film deposited by DCBPMS is more highly (211) oriented (see Fig. 3). So, for the present experiments, the densification of the film due to HIPIM must be significant in order to explain the observed increasing refractive index.

4. Conclusions

Titanium oxide films have been synthesized on steel and glass substrates using conventional DC bipolar pulsed magnetron (DCBPM) and High-Power Impulse Magnetron (HIPIM) sputtering discharges. Electron microscopy has demonstrated the densification of the films when using HIPIM. By X-ray diffraction, crystalline film structures have been determined. Glass substrates are covered by anatase with both techniques.

In magnetron sputtering, rutile is generally obtained by annealing at high temperature (>700–900 °C) [3] or by biasing the substrate with highly negative voltage [4]. In the present study, films deposited on steel substrates with HIPIMS have the rutile

structure while anatase is found for DCBPM. This result is an evidence of a strong energetic condensation process occurring with HIPIM. Rutile is found even on grounded substrates. Another result of this study is that, if steel substrates are bound to a glass slide, i.e. put to the floating potential, anatase appears instead of rutile. This observation is explained by considering the electron and ion fluxes generated by the high-power pulse and their interaction with the substrate. This would bring to light that, in HIPIM sputtering, energetic condensation is not only induced by the high ionization rate of the sputtered vapor but also by the large electron flux reaching the substrate.

In the future it would also be interesting to check if argon is found in large quantities in the films. Discharge gas ions, as they are bombarding the substrate before the metal ions arrive [11], could also be important actors in film crystallization in High-Power Impulse Magnetron deposition processes.

References

[1] A. Mills, S. Le Hunte, J. Photochem. Photobiol., A Chem. 108 (1997) 1.
[2] G. Samsonov, The Oxide Handbook, IFI/Plenum, New York, 1973, p. 333.
[3] N. Martin, C. Russelot, D. Rondot, F. Palmino, R. Mercier, Thin Solid Films 300 (1997) 113.
[4] A. Bendavid, P.J. Martin, H. Takikawa, Thin Solid Films 360 (2000) 241.
[5] J. Alami, P.O.A. Persson, D. Music, J.T. Gudmundsson, J. Bohlmark, U. Helmersson, J. Vac. Sci. Technol. A23 (2005) 278.
[6] W.D. Sproul, D.J. Christie, D.C. Carter, 47th Annual Technical Conference Proceedings, Society of Vacuum Coaters, Albuquerque, 2004, p. 96.
[7] A.P. Ehisarian, W.-D. Munz, L. Hultman, U. Helmersson, I. Petrov, Surf. Coat. Technol. 163–164 (2003) 267.
[8] V. Kouznetsov, K. Macak, J. Schneider, U. Helmersson, I. Petrov, Surf. Coat. Technol. 122 (1999) 290.
[9] S. Konstantinidis, J.P. Dauchot, M. Ganciu, A. Ricard, M. Hecq, J. Appl. Phys. 99 (2006) 13307.
[10] M. Ganciu, M. Hecq, S. Konstantinidis, J.P. Dauchot, M. Touzeau, L. de Poucques, J. Bretagne, World Patent No. WO 2005/090632 (22 March 2004).
[11] S. Konstantinidis, M. Ganciu, J.P. Dauchot, M. Hecq, Appl. Phys. Lett. 88 (2006) 21501.
[12] P.J. Kelly, R.D. Arnell, Vacuum 56 (2000) 159.
[13] J. Sellers, Surf. Coat. Technol. 98 (1998) 1245.
[14] J.T. Gudmundsson, J. Alami, U. Helmersson, Surf. Coat. Technol. 161 (2002) 249.
[15] X.W. Du, B. Wang, N.Q. Zhao, K. Furya, Scr. Mater. 53 (2005) 899.
[16] K. Nakayama, J.H. Weaver, Phys. Rev. Lett. 82 (1999) 980.
[17] J.A. Davis, W.D. Sproul, D.J. Christie, M. Geisler, 47th Annual Technical Conference Proceedings, Society of Vacuum Coaters, Albuquerque, 2004, p. 215.
[18] J. Aarik, A. Aidla, A.-A. Kiisler, T. Uustare, V. Sammelselg, Thin Solid Films 305 (1997) 270.