STUDIA UBB PHYSICA, Vol. 63 (LXIII), 1-2, 2018, pp. 75-88
(RECOMMENDED CITATION)
doi:10.24193/subbphys.2018.07

# OPTIMIZATION OF TITANIUM NITRIDE FILM SYNTHESIS: CORRELATIONS BETWEEN THE STRUCTURE / MICRO-HARDNESS AND DEPOSITION CONDITIONS

**MARIANA POP[1,*], G. NEGREA[1], A. POP[2]**

**ABSTRACT.** The DC sputtering method based on the variation of the potential of target function of nitrogen flow rate, for the deposition of titanium nitride (TiN) films, with the elementary chemical composition close to the stoichiometric one is presented. The process control method used in these experiments is the identification of the nitrogen flow required for the deposition of stoichiometric TiN layers by using the target potential as the reference parameter. The effects of the nitrogen flow, polarization voltage and discharge current on the structure, microstructure and micro-hardness of TiN films was studied.

***Keywords:*** *TiN films, DC sputtering, XRD,hardness.*

## INTRODUCTION

TiN is considered nowadays as one of the most technologically important materials. A wide variety of fabrication techniques have been used for the growth of B1-TiN films, such as Magnetron Sputtering (MS) [1–7].

[1] *Technical University, Faculty of Materials and Environmental Engineering, Bvd.Muncii 103-105, Cluj-Napoca*
[2] *Babeş-Bolyai University, Faculty of Physics, 1 Kogălniceanu str., 400084 Cluj-Napoca, Romania*
[*] *Corresponding author: mariana.pop@ipm.utcluj.ro*

The development of film microstructure in various growth conditions is commonly represented by structure zone models (SZM) [8], which tend to relate the effects of the process parameters on the resulting microstructure of polycrystalline thin film materials. These diagrams are compiled as a function of the homologous temperature, $T_h = T_s/T_M$, where Ts is the substrate temperature and $T_M$ is the melting point of the deposited material ($T_M$ = 3222 K for TiN). For the case of sputter-deposition, it also necessary to take into account the working pressure [9], and more generally the energy deposited per incident particle [10]. Typical deposition conditions to obtain stoichiometric TiN films with a relatively dense microstructure require sufficient adatom mobility. TiN films have high electrical conductivity, adhesion, hardness and chemical inertness therefore they are used as decorative, wear-resistant and corrosion-resistant coatings, for modifying the metal surface against fretting corrosion. Also they are applied in silicon technology as diffusion barriers for aluminum and copper metallization, when creating MOS transistors, ohmic and rectifying contacts. TiN films, exhibit excellent physical and chemical properties combining metal-like and covalent characteristics,such as high electrical conductivity, adhesion, hardness and chemical inertness therefore they are used as decorative, wear-resistant and corrosion-resistant coatings, for modifying the metal surface against fretting corrosion. [11–13].

Some studies have been conducted to investigate the effect of physical parameters on TiN morphology and microstructure as well as electrical properties. Pononetal et.al. [14] found that with increasing nitrogen content, surface roughness,relative intensity of(111)to(200) and film resistivity decrease. Yehetal et al. reported that when sputtering pressure decreases, preferred orientation of TiN films transforms from (111) to (200), and film resistivity decreases while film density increases [15]. The reactive deposition process is considered complex and difficult to control [16, 17], showing maximum instability in the partial nitrogen pressure required to form the stoichiometric layers of nitrides. For the deposition of nitride layers, most of the deposition systems use the partial nitrogen pressure as a control parameter, being maintained within the limits set by the nitrogen flow [16, 18].

Sundgren et al. [19] have shown that at low temperatures due to the low mobility of condensed atoms on the surface of the substrate, the partial pressure range in which stoichiometric layers can be obtained is very narrow and therefore difficult to control. Kuruppu et al. [3] have shown that under conditions of a constant current discharge, the cathode's potential changes depending on the partial pressure of the nitrogen and that it can be used to determine the nitrogen flow required for the deposition of stoichiometric layers. This control method is experimented for depositing layers in the Ti-Si-N system using two magnetrons.

In this work, a simple method of controlling the process of deposition of TiN layers by low temperature reactive DC magnetron sputtering was achieved. The method, based on the variation of the potential of the target according to the nitrogen flow rate, is simple and allows for the quick setting of the conditions required for the deposition of titanium nitride layers with the elementary chemical composition close to the stoichiometric one. The influence of some parameters of the deposition process (nitrogen flow, polarization voltage, discharge current) on the microstructure and layer microstructure on the TiN films was studied.

## EXPERIMENTAL

The DC magnetron sputtering system was installed in confocal geometry with two debit-meters; one with neutral Ar gas and other with nitrogen ($N_2$) reactive gas. The magnetrons was inclined with 24 degrees between their symmetry axes. The Si (001) single crystalline substrate with the size of 25x15x0.54 mm is heated (reaching a maximum temperature of 700 ° C) and a thermo-regulator controls the substrate temperature. The substrate was ultrasonically cleaned in trichlorethylene, acetone and then methanol. A titanium target of 99.95% purity was used. The deposition was carried out at a pressure of 0.66 Pa (5 mTorr) under Ar + $N_2$ atmosphere at a 6 Amper discharge current. The substrate temperature of was measured by using a chromium-aluminum thermocouple in direct contact with it. As the

films were not heated further, their temperature did not exceed $200^0$ C at the end of the deposition. The installation also contains a flat electromagnetic probe of Langmuir type, mounted on a support behind the substrate and having the same dimensions as the substrate. An auxiliary coil is located behind the substrate support. The role of the Langmuir sample is to characterize the plasma in the substrate area, and the role of the coil is to modify the magnetic field distribution and, implicitly, the trajectory of charged particles (ion and electron flow) into the film deposition area on the substrate. The structural analysis of deposited layers was done by the X-ray diffraction (XRD) in the Bragg-Brentano configuration. The radiation used was Cu $K_{\alpha 1}$, the acceleration voltage of 40 kV and the current of 30 mA. The tests were carried out with a step of $0.02^o$ in $2\theta$ and a counting time of 2 sec / step. The micro-hardness measurements were made with 0.1 N load, on layers with thicknesses in the range of 3.9-4.2 $\mu$m, deposited on Si substrate. Determinations were made using the Vickers method. Because weights of less than 1.96 Newton were used, the notion of micro-hardness was used.

## RESULTS AND DISCUSSIONS

### A. Controlling and adjusting the deposition process

The classical method for controlling cathodic sputter deposition processes is based on the measurement and adjustment of the partial pressure of reactive gas (nitrogen or oxygen), depending on the nature of the deposition layer. Reactive cathodic sputtering deposition leads to complex phenomena on the surface of the target. As the reactive gas flow increases, the target surface is covered with a compound layer, which has other characteristics compared to the target material. The sputtering yield decreases, implicitly decreasing the deposition rate and prolonging the time required to achieve a layer of a certain thickness. Figure 1 shows the dependence of the target potential ($V_T$) function of the nitrogen flow ($\Phi_{N2}$) recorded for a discharge current $I_d$ = 6 A at a partial argon pressure $p_{Ar}$ = 0,66

Pa (5 mTorr) and a voltage polarization of the substrate Vs =- 20 V. It is noted that this curve has a maximum ($V_{Tmax}$), which, for the specified conditions, has a value of ≈550 V and corresponds to a nitrogen flow $\Phi_{N2} \approx 6,4$ cm$^3$ / min. The tests performed showed that this peak is associated with nitrogen flow around which Ti layers with stoichiometry close to the theoretical (atomic ratio N / Ti = 1) can be deposited.

The optimal deposition regime is close to the point where the partial pressure of the active gas tends to rise rapidly (point B in figure 1).

The process control method used in these experiments is based on the rapid identification of the nitrogen flow required for the deposition of stoichiometric TiN layers by using the target potential as the reference parameter.

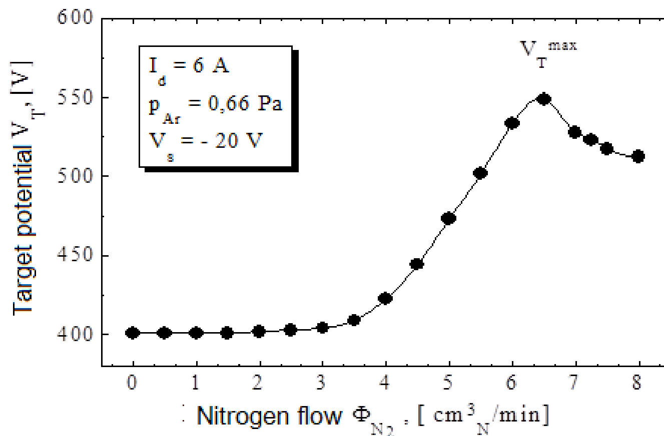


**Figure 1.** Variation of target potential according to nitrogen flow in constant current discharge mode.

By correlating the data regarding the variation of the potential of the target with those related to the variation of the partial pressure of nitrogen according to the nitrogen flow, the following conclusions can be drawn:

- For nitrogen flow rates less than ≈ 4 cm$^3$ / min, the cathodic sputtering is done in a metallic regime, for nitrogen flow rates higher than ≈ 7.5 cm$^3$ / min, the sputtering is in the compound mode and for flows in the range 4-7 cm$^3$ / min there is a transient regime.

- The transition from preferential metal deposition (RM) to predominantly compound (RC) deposition takes place within the critical range (IC) $\Phi_{N\,2} \approx$ 6-7 cm$^3$ / min and is characterized by a more pronounced increase in pressure partial nitrogen.

Within this range, the nitrogen flow required to deposit layers with composition as close to stoichiometric as possible, but without passing through (RC) should be determined.

- Increase of partial nitrogen pressure in (IC) is $\Delta p_{N2\,cd}$ = 0,26 mTorr (0,035 Pa), a very narrow pressure range, which, in order to be used as process parameter, requires special measuring means.

- The target potential variation in the (IC) is $\Delta V_T \approx$ 17 V, a variation easily measurable with ordinary devices. In addition, unlike the partial pressure $p_{N2cd}$, which increases continuously in (IC), the potential of the target exhibits a peak ($V_{Tmax}$), which makes the area (IC) very fast and accurate.

- This process control method, based on monitoring the variation of the potential of the target according to the nitrogen flow (with an X-Y coordinate recorder under the experimental conditions imposed here), is particularly simple and proved to be effective.

In order to study the microstructure of layers obtained using the $V_T$ = f ($\Phi_{N\,/\,2}$) curve as the process regulating tool, two series of depositions were made at two different polarization stresses at the characteristic points of this curve, marked with A, B, C and $A_1$, $B_1$, $C_1$ according to figure 1.

Layers deposited at lower nitrogen flow rates (e.g., 3.4 cm $^3$/ min) did not show the gold color specific for TiN nitrides but were white to yellow in color, indicating a high nitrogen deficiency.

Using nitrogen flows with values ranging from 5-8 cm$^3$ / min, we obtained films where the Ti / Ni ratio tends to the unit.

Deposition conditions were: discharge current $I_d$ = 6 A and argon pressure $p_{Ar}$ = 0,66 Pa (5 mTorr). Table 1 lists the other deposition conditions as $V_T$ of target potential and the values of the Vs substrate potential. Knowing the deposition time and the thickness *h* of the deposited layers we determined the deposition rate.

**Table 1.** Nitrogen flow $\Phi_{N2}$, $V_T$ of target potential, Vs of substrate polarization voltage, deposition time t, layer thickness h, and $v_d$ deposition rate for sample series A, B, C and A1, B1, C1, deposited in the appropriate points marked in figure 1.

| Sample | $\Phi_{N2}$ cm$^3$/min | $V_T$ Volt | $V_s$ Volt | t min | h μm | $v_d$ μm/h |
|---|---|---|---|---|---|---|
| A | 5,0 | 472 | -25 | 10 | 1,68 | 10,08 |
| B | 6,2 | 540 | -25 | 10 | 1,65 | 9,90 |
| C | 8,0 | 507 | -25 | 10 | 0,95 | 5,70 |
| $A_1$ | 5,0 | 470 | -350 | 10 | 1,35 | 8,10 |
| $B_1$ | 6,2 | 540 | -350 | 10 | 1,30 | 7,80 |
| $C_1$ | 8,0 | 500 | -350 | 15 | 1,00 | 4,00 |

Figure 2 shows the dependence of film deposition rate function of nitrogen flow rate, for the two series of samples. It is noted that the deposition rate decreases quite rapidly with the increase of the nitrogen flow above the maximum value of the $V_T = f(\Phi_{N2})$ curve, indicating the coverage of the target surface with a layer of TiN and the change of the sputtering rate.

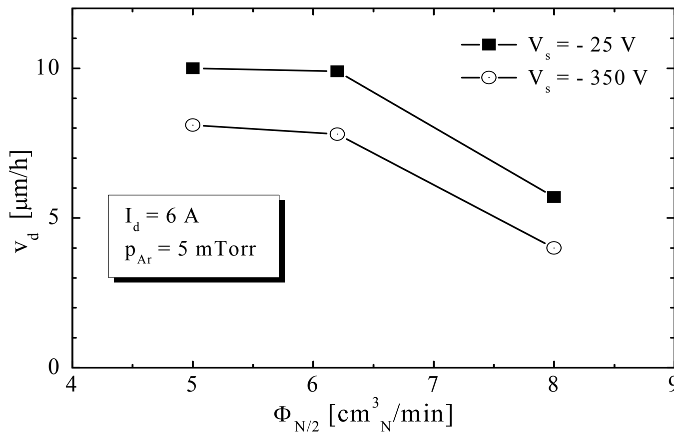


**Figure 2.** Dependence of the deposition rate $v_d$ vs. the nitrogen flow $\Phi_{N2}$, for two polarization voltage of the substrate: -25 and - 350 V.

Film deposition of sample B was made at a nitrogen flow slightly lower than that corresponding to the peak curve $V_T = f(\Phi_{N\,2})$ in order to avoid passing the discharge in compound mode.

Irrespective of the nitrogen flow rate used, the deposition rate is reduced by approximately 20% by increasing the polarization voltage of the sample from -25 V to -350 V. More probably the decrease of the deposition rate is due to the re-sputtering of N and Ti atoms deposited as a result of higher energy of ion bombardment and densification of the deposited layer. The deposition rate is reduced by approximately 20% by increasing the polarization voltage of the sample from -25 V to -350 V.

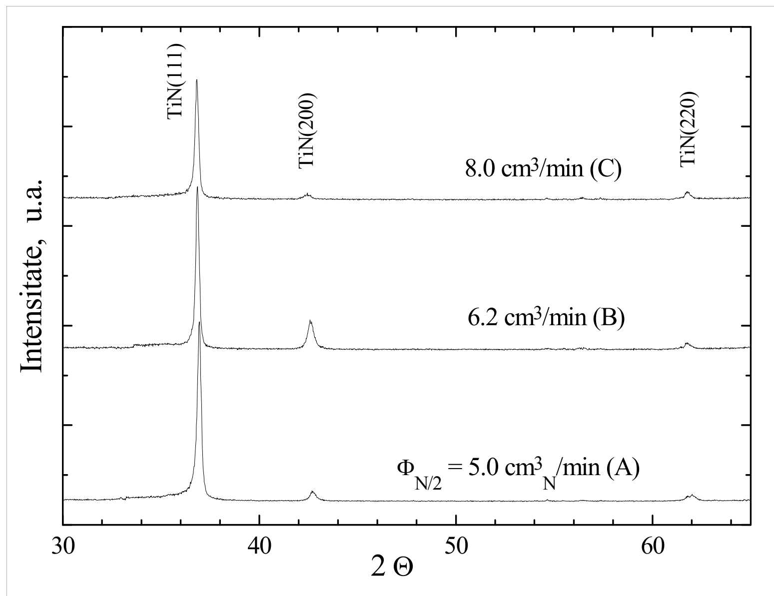


**Figure 3.** The XRD spectrum of samples A, B and C (see Table 1).

Figure 3 shows the X-ray diffraction measurements spectra for the samples A, B, C deposited at a polarization voltage of -25 V. It is noted that the increase in the nitrogen flow rate from 5.0 to 8.0 $cm^3$/min does not affect the phase composition of the deposited layers. The relative ratio of line intensities in the diffraction spectra indicates a pronounced preferential

crystallographic orientation (111) compared to the standard spectrum of TiN powder. The tendency for preferential orientation of TiN grains is slightly lower for the layer deposited at the maximum point of the curve $V_T$ = f (Ň$_{N / 2}$), (sample B). The TiN films deposited under relatively low intensity bombardment conditions have surface chemistry processes that favour the formation of [111] preferential orientation [20]. Therefore, based on the analysis of X-ray patterns it can be concluded that the nitrogen flowrate has stronger impact on the film properties when the current density is higher [21].

XRD show that all 6 samples, deposited at nitrogen flows around the maximum point of the $V_T = f(\Phi_{N / 2})$ curve, show only the peaks of the TiN compound.

A significant difference was found between the XRD spectra of the $A_1$, $B_1$, and $C_1$ series samples compared to those of the A, B, C series samples. Figure 4 shows the XRD spectra for the samples B and $B_1$ deposited at a polarization voltage of -25 V and -350 V, and obtained at peak curve points $V_T = f((\Phi_{N2})$, respectively.

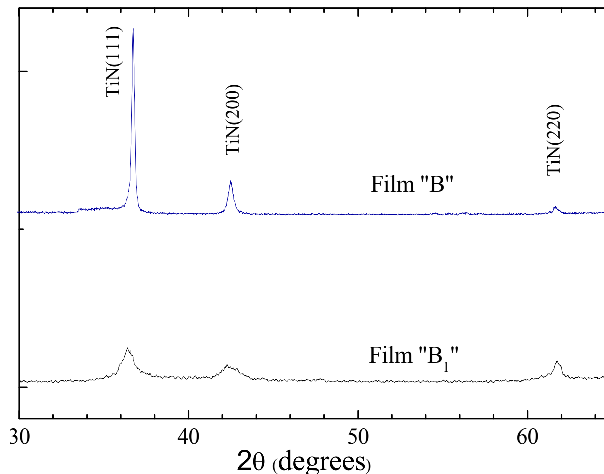


**Figure 4.** XRD for samples B and B1 (see Table 6.1).

The diffraction peaks of sample $B_1$ shows a low intensity and a wide line width at half intensity. The decreasing of the intensity peaks and widening them by increasing the polarization voltage of the sample from -

25 V to -350 V suggest the increase of the defects density of the TiN layer, the reducing of the average grain size and the increase of the remaining tensions in the film.

The examination of the color of the layers deposited at different nitrogen flows in the range 3.4 - 8.0 $cm^3$ / min showed that the films deposited at:

- nitrogen flows lower than the maximum flow rate $V_T = f(\Phi_{N2})$ have lighter colors indicating sub-stoichiometric compositions (N /Ti < 1.0);

- the maximum point of the curve $V_T = f(\Phi_{N/2})$, respectively B and $B_1$ have a titanium nitride-specific golden color;

- nitrogen flows higher than the flow corresponding to the maximum curve VT = f (ΦN / 2) are darker to brown, indicating over-stoichiometric compositions (N /Ti > 1.0).

Figure 5 shows the dependence of micro-hardness function of the nitrogen flow of the TiN films. The maximum value of the micro-hardness obtained was 1930 HV0,01, somewhat lower than the reference value of TiN hardness in the literature (2200 HV). This difference could be due to the presence of micro-pores in the layer structure.

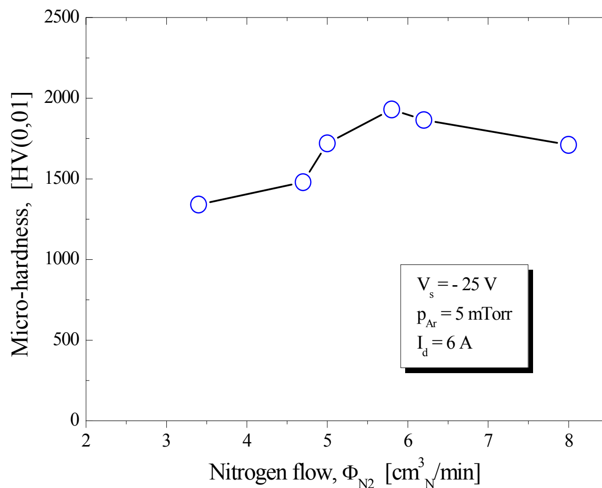


**Figure 5.** Variation of micro-hardness of TiN layers according to nitrogen flow.

The micro-hardness increases rapidly from 1520 to 1870 HV0,01 with the increase of the polarization voltage from Vs = - 25 V to -150 V. For Vs = -350 V, a micro-hardness of 1950 HV0,01 is obtained. These results show that the micro-hardness of the TiN layers increases with increasing the polarization stress of the substrate, but for the deposition of higher hardness layers, it is not necessary for the deposition system to be modified to allow not only the increase in the ion flux density of their energy.

**B. Checking the control / process control solution**

In order to check the viability of the method applied for controlling / adjusting the process, in figure 6, the characteristic curves $V_T = f(\Phi_{N/2})$ for the three discharge currents are recorded for: 2 A, 4 A and 6A. It can be seen that even in the case of lower discharge currents, the $V_T = f(\Phi_{N/2})$ curves have well-defined maxima which can be used for rapid determination of the nitrogen flow over which the cathodic sputtering lead to stoichiometric TiN films.

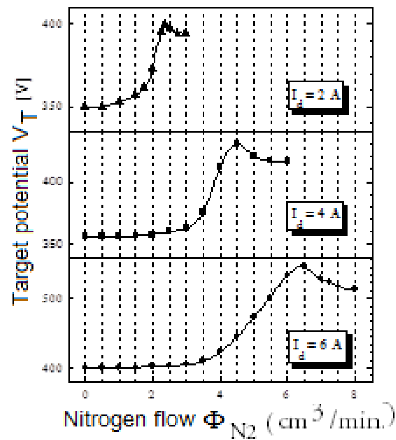


**Figure 6.** Characteristic curves $V_T = f(\Phi_{N/2})$ for three different values of the discharge current $I_d$=2; 4 and 6 A ($p_{Ar}$ = 0,66 Pa).

For the lower discharge current (2 A), a film was deposited on the silicon substrate under the following conditions: $p_{Ar}$ = 0.66 Pa; $\Phi_{N/2}$ = 2.2 cm3 N / min;

($V_T = V_{Tmax}$ for $\Phi_{N/2} = 2.3$ cm$^3$ / min); $V_T = -393$ V; Vs = - 25 V; time deposition 10 min. The thickness of the layer was determined to be 0.48 µm, resulting in a deposition rate of approx. 2.9 µm / hr. The color of the deposited layer was identical to that deposited on sample B indicating very close N/Ti atomic ratios. Figure 7 shows the XRD peaks of film obtained by using a current of 2A. It is noted that only the TiN diffraction lines appear in the XRD spectrum, and that ratio of the intensity of the diffraction lines (111) / (200) / (220) is similar to sample B.

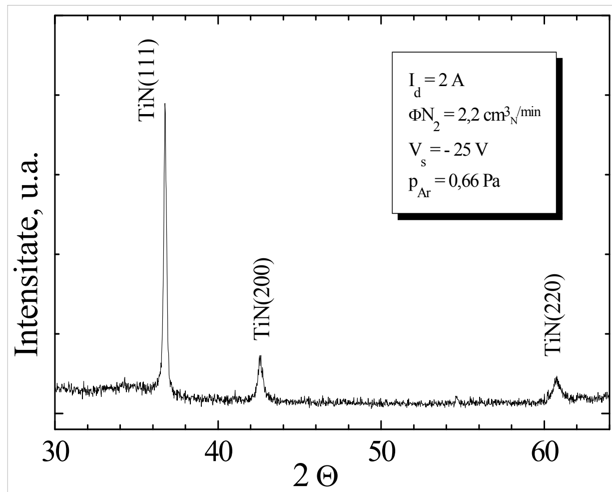


**Figure 7.** XRD of TiN film deposited at a discharge current $I_d$ = 2 A.

The obtained results confirm the viability of the method used to regulate the deposition process of the TiN layers in the constant discharge mode.

## CONCLUSIONS

DC sputtering method, based on the variation of the potential of the target according to the nitrogen flow rate, is simple and allows for the quick setting of the conditions required for the deposition of titanium nitride films with the elementary chemical composition close to the stoichiometric one.

The parameters of the deposition process (nitrogen flow, polarization voltage, discharge current) influenced microstructure and the micro-hardness of the TiN films. The correlations between the structure / micro- hardness and deposition conditions was evidenced.

The maximum hardness of the TiN layers obtained was slightly lower than that reported by other authors. A likely explanation hardness values TiN films obtained is the low deposition temperature, is the formation of columnar structures with a low compaction degree.

## REFERENCES


1. L. Hultman, S.A. Barnett, J.E. Sundgren, J.E. Greene, *J. Cryst. Growth* 92, 639–656 (1988).
2. W.D. Sproul, P.J. Rudnik, M.E. Graham, S.L. Rohde, *Surf. Coat. Technol.* 43, 270–278 (1990).
3. M. L. Kuruppu, G. Negrea, I. P. Ivanov, and S. L. Rohde, *Journal of Vacuum Science and Technology A*, 16(3),1949-1955 (1998).
4. P. Patsalas, C. Charitidis, S. Logothetidis, *Surf. Coat. Technol.* 125, 335–340 (2000).
5. P.H. Mayrhofer, F. Kunc, J. Musil, C. Mitterer, *Thin Solid Films* 415, 151– 159 (2002).
6. G. Abadias, P. Guerin, *Appl. Phys. Lett.* 93, 111908 (2008).
7. S. Mahieu, D. Depla, *J. Phys. D: Appl. Phys.* 42, 053002 (2009).
8. S. Mahieu, P. Ghekiere, D. Depla, R. De Gryse, *Thin Solid Films* 515, 1229 (2006).
9. J.A. Thornton, *J. Vac. Sci. Technol. A* 4, 3059–3065 (1986).
10. A. Anders, *Thin Solid Films* 518, 4087–4090 (2010).
11. R.Kröger, M.Eizenberg, C.Marcadal, L.Chen, *J.Appl.Phys*.91, 5149–5154 (2002).
12. Z.Peng, H.Miao, L.Qi, S.Yang, C.Liu, *ActaMater*.51, 3085–3094 (2003).
13. R.W.Poon, J.P.Ho, X.Liu, C.Chung, P.K.Chu, K.W.Yeung W.W. Lu, K.M.Cheung, *Thin Solid Films* 488, 20–2 (2005)
14. N.K.Ponon, D.J.Appleby, E.Arac, P.King, S.Ganti, K.S.Kwa, A. O'Neill, *Thin Solid Films* 578,31–37 (2015)

15. T.-S.Yeh, J.-M.Wu, L.-J.Hu, *Thin Solid Films* 516, 7294–7298 (2008).
16. B. Window, *Surface and Coatings Technology*, 81(1), 92-98 (1996).
17. J. Musil, S. Kadlec, J. Vyskočil, V. Valvoda, *Thin Solid Films*, 167(1-2), 107-120 (1988).
18. M. Ohring, "The Materials Science of Thin Films", Academic Press, New York, (1992).
19. J. -E. Sundgren, B.O. Johansson, A. Rockett, S.A. Barnett, J.E. Greene, „American Institute of Physics- Conference Proceedings", 149, 95-115 ,(1996).
20. J.C. Oliveira, F. Fernandes, R. Serra, A. Cavaleiro, *Thin Solid Films* 645, 253-264 (2018). 21. A A Kozin, V I Shapovalov, V V Smirnov, A S Useinov,K S Kravchuk, E V Gladkikh, A V Zavyalov and A A Morozova , IOP Conf. Series: *Journal of Physics: Conf. Series* **872** (2017) 012019