TITANIUM NITRIDE FILM DEPOSITION ON GLASS SURFACE ON CATHODIC CAGE PLASMA DPOSITION

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Abstract. *The cathodic cage is an adaptation of ionic nitriding that was developed at Labplasma (Laboratório de Processamento de Materiais por Plasma) in UFRN (Universidade Federal do Rio Grande do Norte) in order to reduce undesirable problems of the conventional technique. That new technique allows to obtain a more homogeneous film, which is evidenced by a uniform hardness throughout the sample due to the edge effect reduction, the hollow cathode effect reduction and the reduction of voltaic arcs. In order to study the plasma atmosphere influence and deposition time on the obtained film, it was used a titanium cathodic cage because of its chemical and heating susceptibility. The titanium nitride was deposited on glass surface utilizing an atmosphere composed by argon, hydrogen and nitrogen in different proportions. The active species into the plasma were analyzed by Optical Emission Spectroscopy and the obatined TiN film was analyzed by Grazing Incidence X-Ray Diffraction. It is noticed that through the cathodic cage deposition it is possible to obtain a TiN film on glass surface.*

Keywords: *Cathodic cage, TiN thin film, plasma deposition.*

1. INTRODUCTION

The titanium nitride films become known for their use on steels as way of increasing of superficial hardness and improvement in the anticorrosive properties. Those films are often used in cutting tools, because of their properties as hardness, mechanical and corrosion resistance (Veprek, 1999). Recently, it has been studied other applications for TiN films, exploring mainly their optical properties. TiN films are deposited on glass surface to be used as a clear solar control window to save energy in both cooling and clearing. Moreover, both their conductive characteristics and wave selective transparent optical properties have promoted the use of TiN films as transparent electrodes in solar cells and light-emitting diodes (Uen, 2007 and Tarniowy, 1997).

There are various plasma techniques for film deposition. Among those techniques, the magnetron sputtering (Jeyachandran, 2007) and cathodic cage coupled in nitride plasma reactor (Sousa, 2009) have been studied because of the interesting properties obtained in films deposited and the technique versatility.

The cathodic cage is an ionic nitriding adaptation developed in order to reduce the defects generated by conventional technique. It was developed at Labplasma – UFRN in Brazil. The cathodic cage consists of a cylindrical plate with holes and a cylindrical covering with similar holes. In this configuration, the cage acts as a cathode which is applied the electrical potential difference in relation to the chamber walls. Thus, the sputtering process happens on the cage avoiding damages on the surface of the sample. The sputtered atoms can be bonded with reactive particles of plasma and they are deposited on the sample surface (Sousa, 2008 and Ahangarani, 2009). Moreover, that technique allows obtaining a more homogeneous film, which is evidenced by a uniform hardness throughout the sample. That uniformity may be motivated for the edge effect, voltaic arcs and hollow cathode effect reduction (Gallo, 2010 and Hubbard, 2010).

Using cathodic cage it is possible to nitride a metallic surface, but also it is possible to obtain film deposited, since there is material sputtered from the cage which may be bonded with the active species of the plasma and the product are arranged on the sample surface (Araújo, 2008).

Since the titanium nitride film importance and their large application possibilities, it was made a titanium cathodic cage for obtaining titanium nitride thin film on glass surface. For this case, some difficulties may occur due to oxide layer formed on the titanium surface. Thus, some care must be taken to avoid as much as possible the cage contamination for oxide, such as pre-sputtering process.

It has been obtained TiN thin films on glass surface utilizing different plasma atmosphere conditions and different deposition time. In order to investigate the plasma active species influence in deposited film properties, the process was monitored by Optical Emission Spectroscopy (OES). The obtained film was analyzed by Grazing Incidences X-Ray Diffraction (GIXRD).

2. EXPERIMENTAL

The experimental setup used in this work is a rectangular glass sample with 2 mm thickness, 20 mm length and 20 mm width. The samples were cleaned in an ultrasonic bath using acetone p.a. Then, the samples were dried using a hot air current around 60 ºC.

The conventional ionic nitriding chamber was adapted to the cathodic cage plasma deposition configuration which consists of a vertically mounted cylindrical vacuum chamber (300 mm in diameter and 300 mm in height, made of stainless steel) held at ground potential and a high voltage DC source (maximum output 1500 V, 1.5 A). In the main cylinder there is a window made of glass (quartz). Into the reactor located on the cathode it was placed the cathodic cage. It is made of commercially pure titanium. The cage has 70 mm diameter, 42 mm height and 1 mm thickness; it has 45 hollows of 8 mm in diameter that are distributed as show in figure 1. The distances between the centers of holes are 9.2 mm. The cage covering has 70 mm diameter with 9 holes of 8 mm diameter that is distributed in a cross shape. The sample was placed on an isolating (alumina disc of 60 mm diameter and 2 mm thickness). In the inferior flange, there are several connections for the pressure measurement by a sensor, gas inlet and outlet. The gas flow is controlled by flow controllers (MKS MFC1179A). The superior and inferior extremities of the main cylinder are closed utilizing L gaskets and the flanges.

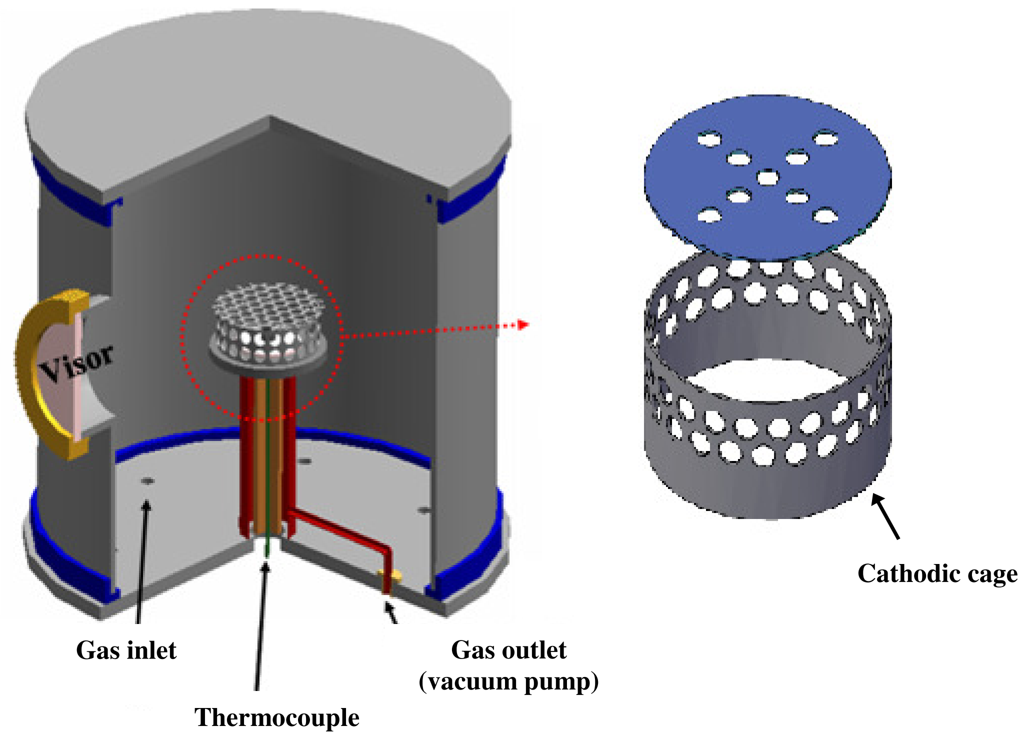

Figure 1. Schematic representation of ionic nitriding reactor adapted to the cathodic cage configuration highlighting cathodic cage detail

Four deposition processes were performed in the following conditions: 10 sccm of N_2 gas flow for 180 minutes, 10 sccm of 80% N_2 – H_2 gas flow for 60 minutes, 9 sccm of 33.3% N_2 – 44.4% Ar – H_2 gas flow for 45 and 120 minutes. The pressure and the temperature were maintained constant at 2 mbar and 450 ºC, respectively. Before treatments, a pre-sputtering was carried out utilizing H_2 gas flow of 8 sccm at 1 mbar and 200 ºC, for 30 minutes.

Those deposition treatments were monitored by Optical Emission Spectroscopy (OES) to verify the present species into the plasma during the deposition process. The OES system is an Ocean Optics USB 40000 spectrograph with optical resolution of 0.3 at 10 nm, focal length of 42 mm input and 62 mm output and optical response between 200 – 1100 nm.

The X-Ray Diffraction was performed by a Schimadzu XRD – 6000 diffractometer, with accessory for Grazing Incidence X-Ray Diffraction (GIXRD) prepared for thin film analysis.

3. RESULTS AND DISCUSSIONS

3.1. Optical Spectroscopy Emission (OES)

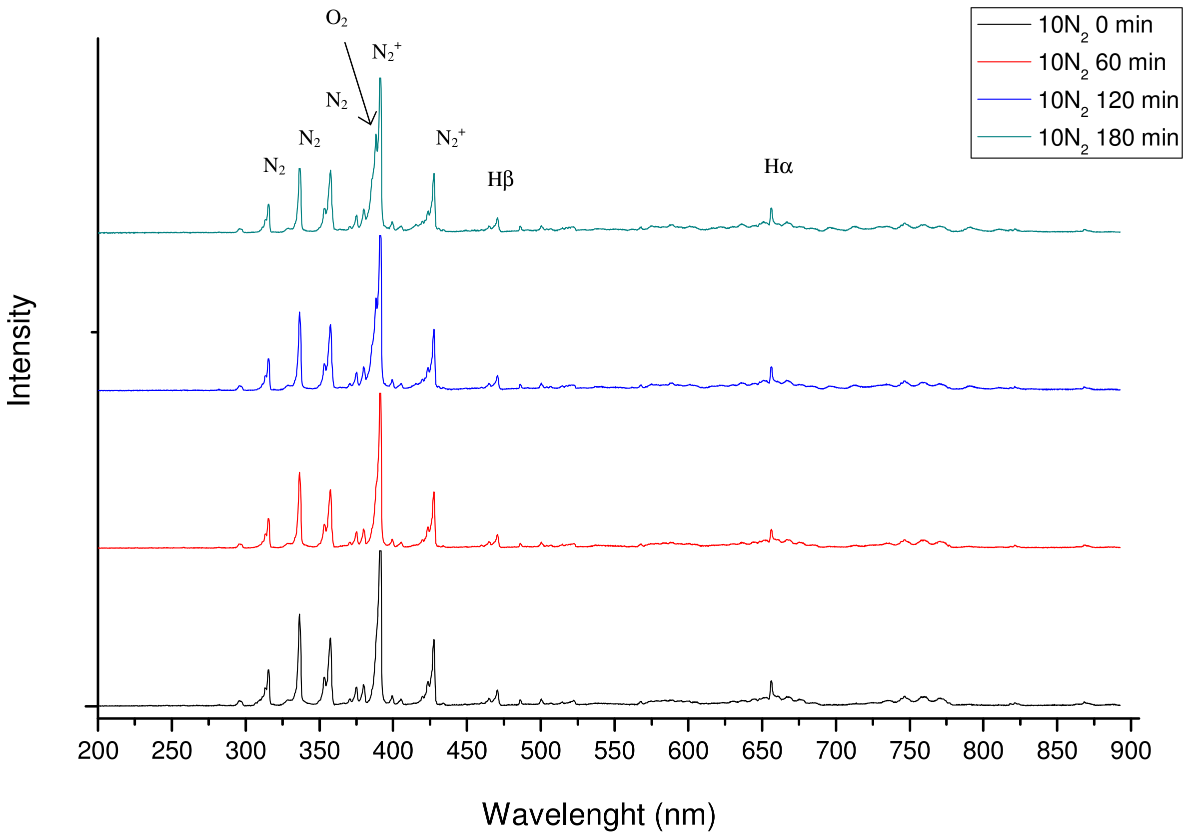

Figure 2. Plasma spectra in cathodic cage deposition process in different treatment time at 450 º C, 2 mbar and 10 sccm of N_2 gas flow

The figure 2 shows the obtained spectra in different deposition times in processes with 10 sccm of N_2 gas flow at 450 ºC. It is possible to identify the peaks corresponding to N_2, N_2^+, Hα, Hβ and O_2 wavelength.

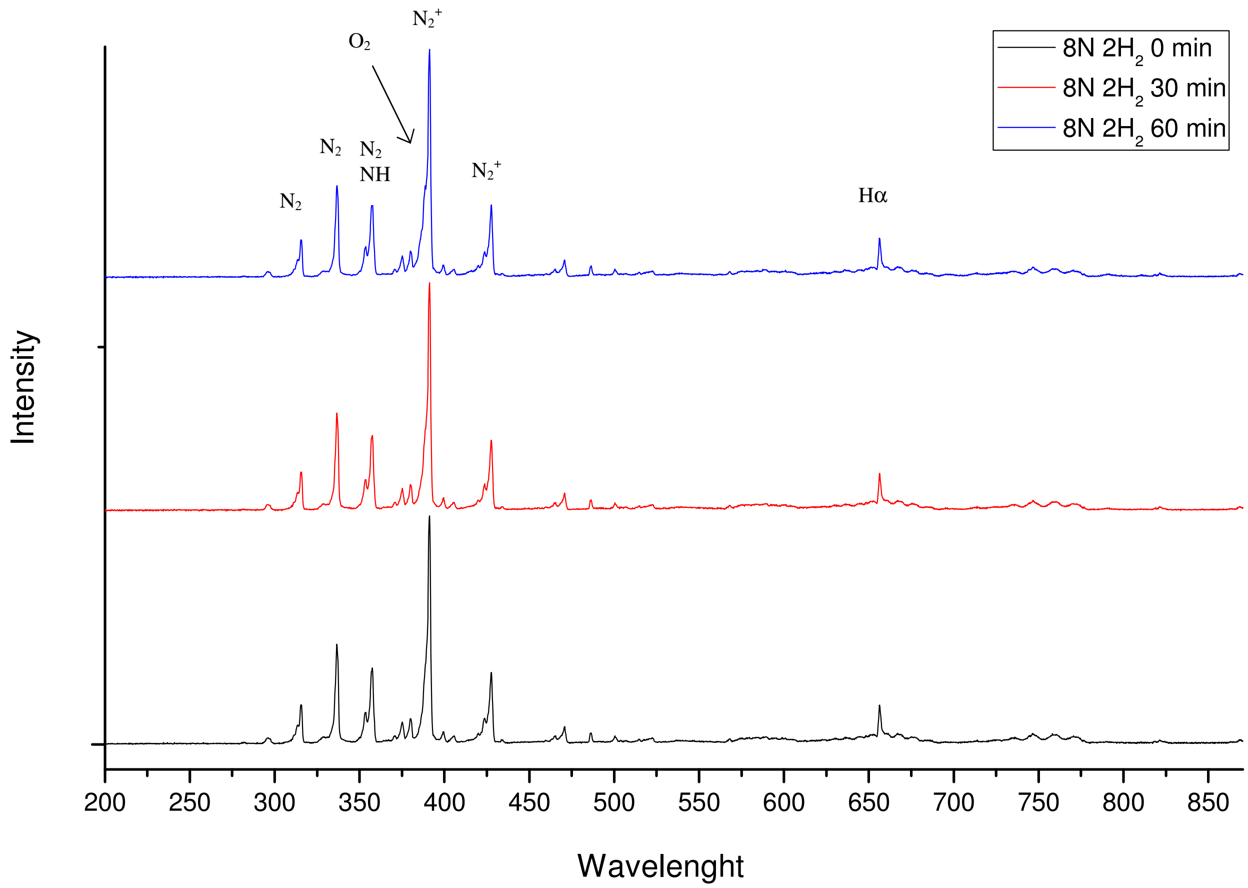

Figure 3. Plasma spectra in cathodic cage deposition process in different treatment time at 450 º C, 2 mbar and 10 sccm of 80% $N_2 - H_2$ gas mixture

The figure 3 presents the obtained spectra in deposition process utilizing 80% $N_2 - H_2$ plasma mixture in different times at 450 ºC. It is possible to identify the peak corresponding to N_2, N_2^+, O_2, NH, Hα and Hβ wavelength.

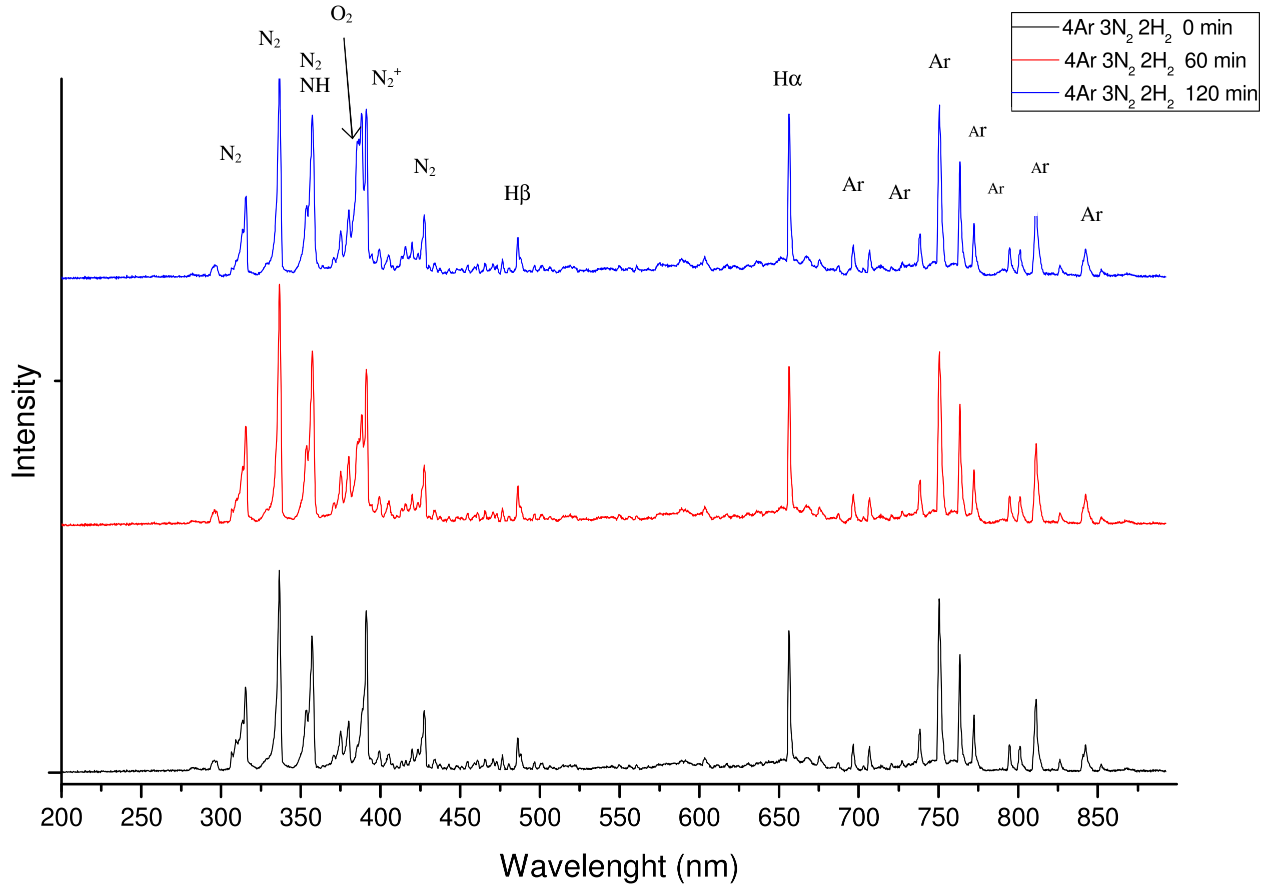

Figure 4. Plasma spectra in cathodic cage deposition process in different treatment time at 450 º C, 2 mbar and 9 sccm of 33.3% N_2 – 44.4% Ar – H_2 gas mixture

The figure 4 presents the obtained spectra in deposition process utilizing 33.3% N_2 – 44.4 % Ar – H_2 plasma mixture in different times at 450 ºC. It is possible to identify the peak corresponding to N_2, N_2^+, O_2, NH, Hα, Hβ and Ar wavelength.

In the spectra of figure 4, it is noticed that the peak referent to Hα is more intense than the others, which may be attributed to the presence of argon. Because of that the number of electron and consequently collision among electron and other particles increases, exciting hydrogen atoms.

In all spectra presented above, there is a peak increasing with the reaction time. This peak probably is related to O_2 molecule, since the ionic bombardment on the cage sputters the oxygen particles and TiO_2 compounds inserted into the material. The peak associated to O_2 specie grows more in the plasma atmosphere containing argon because that gas is inert and the O_2 species sputtered remain free while the plasma containing H_2 gas is totally reactive increasing the bond rate.

3.2. Grazing incidence x-ray diffraction

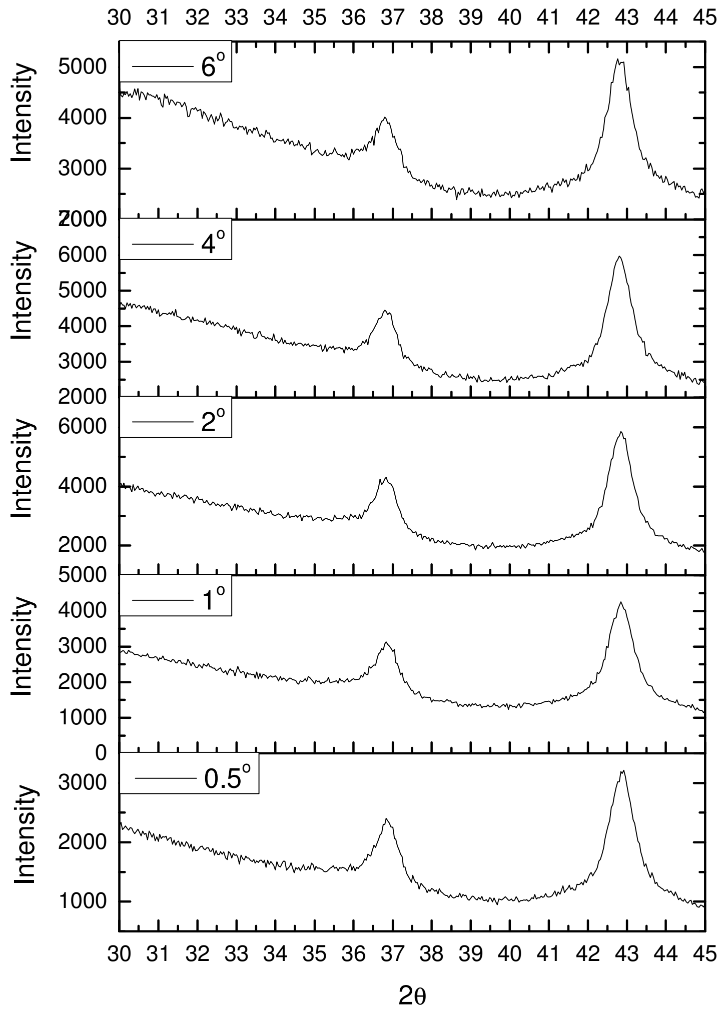

Figure 5. XRD pattern for TiN film obtained in 10 sccm of N_2 gas mixture in 180 minutes. The different grazing angles were indicated in the figure

The figure 5 shows the diffractogram for obtained sample in 10 sccm of N_2 gas flow. It was possible to identify two peaks related with δ-TiN phase, from the 38-1420 XRD letter. The peak with 2θ in 32.66º is referent to a δ-TiN (1 1 1) phase and the peak with 2θ in a 42.60º is reference to δ-TiN (2 0 0) phase.

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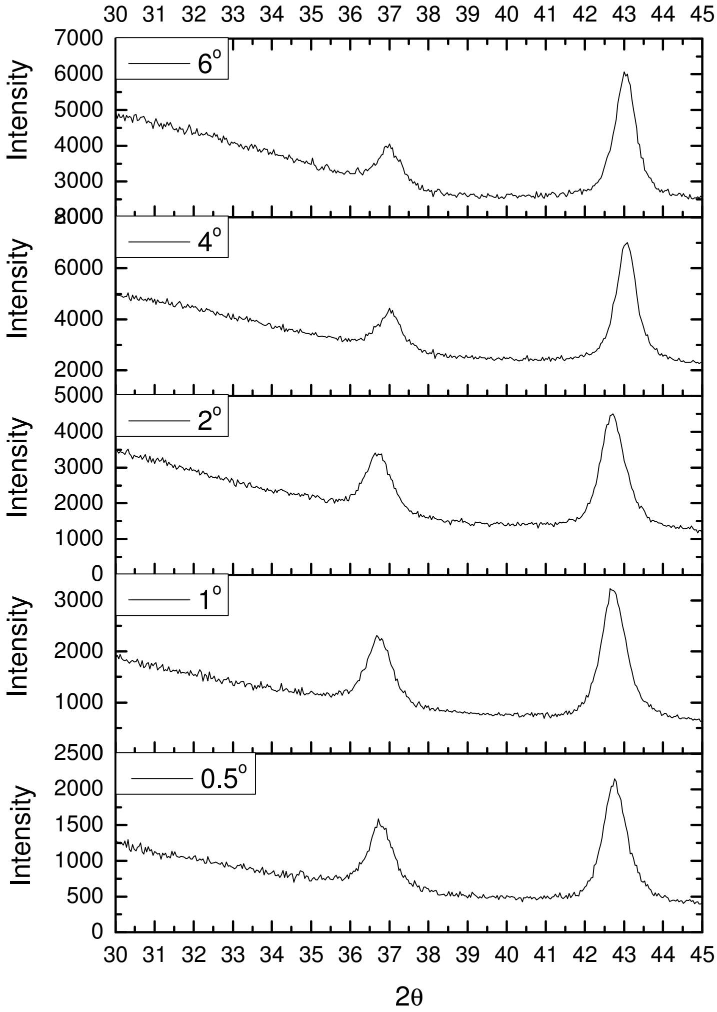


Figure 6. XRD pattern for TiN film obtained in 10 sccm of 80% $N_2 - H_2$ gas mixture in 60 minutes. The different grazing angles are indicated in the figure

The figure 6 presents the XRD pattern for obtained sample in 10 sccm of 80% $N_2 - H_2$ gas flow. It was possible to identify two peaks related with δ-TiN phases. The peak with 2θ in 32.66º is reference to a δ-TiN (1 1 1) phase and the peak with 2θ in a 42.60º is referent to δ-TiN (2 0 0) phase. However, the peaks in some grazing angles have a small shift, when it is compared with XRD letter peaks, which could be explained by residual stress in the film.

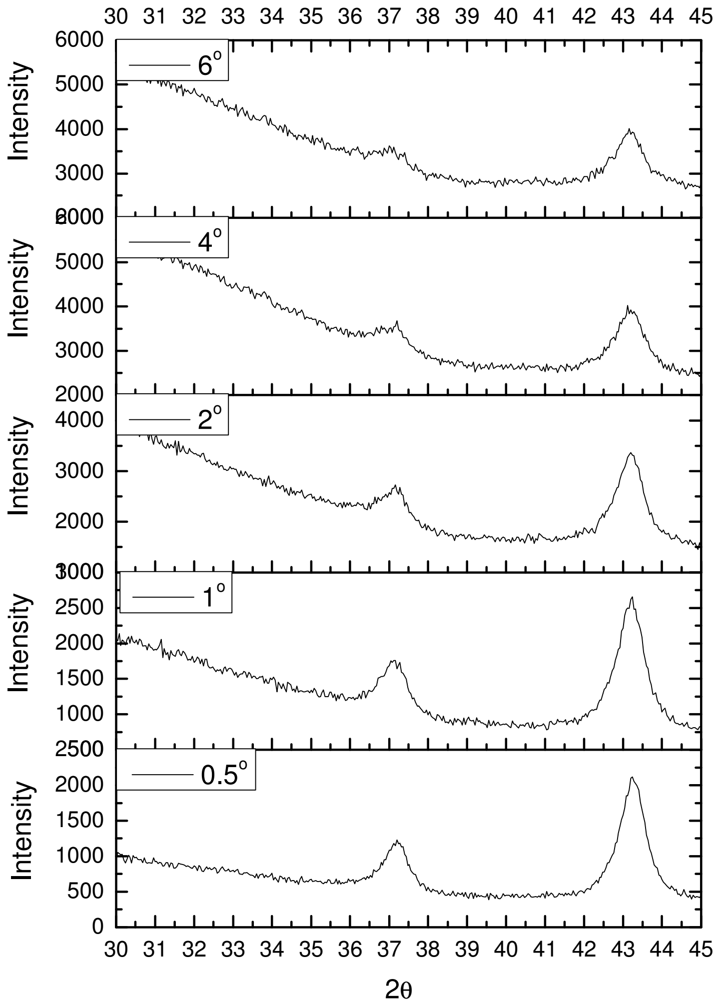


Figure 7. XRD pattern for TiN film obtained in 9 sccm of 33.3% N_2 – 44.4% Ar – H_2 gas mixture in 45 minutes. The different grazing angles are indicated in the figure

The figure 7 shows the XRD pattern for obtained sample in 9 sccm of 33.3% N_2 – 44.4% Ar – H_2 gas mixture, for 45 minutes at 450 ^oC. It was possible to identify two peaks related with δ-TiN phase. The peak with 2θ in 32.66º is referent to the δ-TiN (1 1 1) phase and the peak with 2θ in a 42.60º is referent to the δ-TiN (2 0 0) phase.

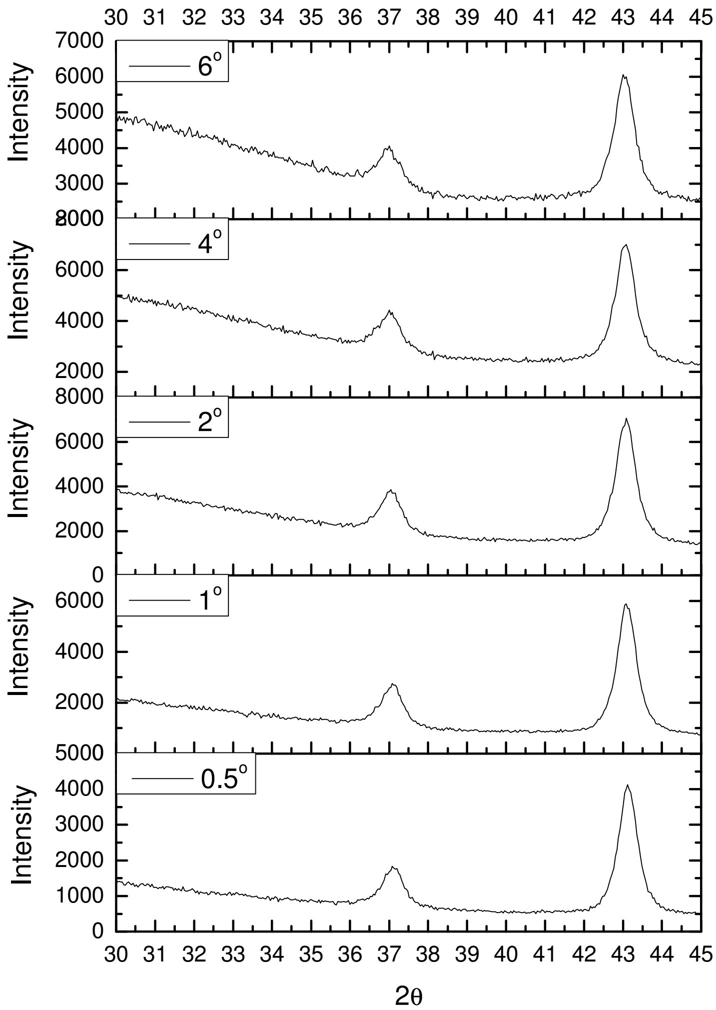
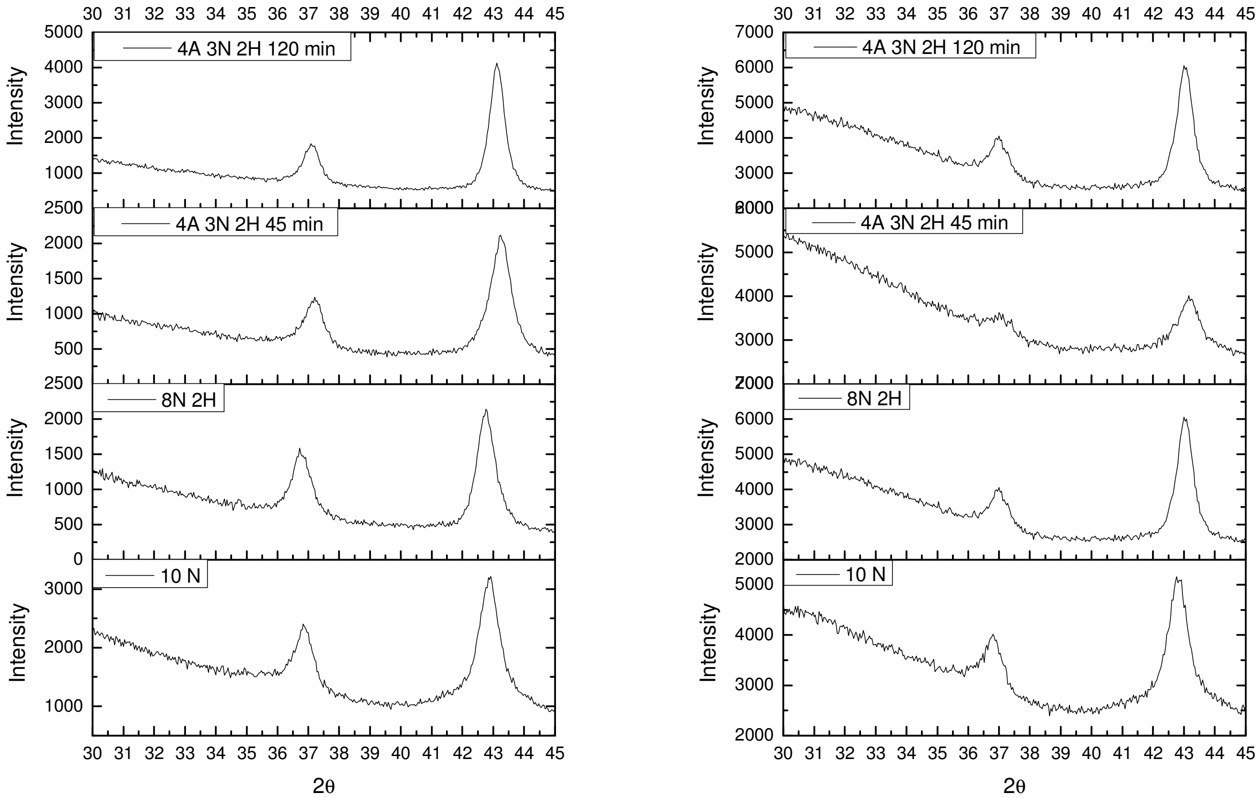


Figure 8. XRD pattern for TiN film obtained in 9 sccm of 33.3% N_2 – 44.4% Ar – H_2 gas mixture in 120 minutes. The different grazing angles are indicated in the figure

The figure 8 presents the XRD pattern for obtained sample in 9 sccm of 33.3% N_2 – 44.4% Ar – H_2 gas mixture at 450 ^oC for 120 minutes. It was possible to identify two peaks related with δ-TiN phases. The peak with 2θ in 32.66° is reference to a δ-TiN (1 1 1) phase and the peak with 2θ in a 42.60° is referent to δ-TiN (2 0 0) phase. Comparing both XRD of figures 7 and 8, it is remarkable that the peaks are higher in the pattern of figure 8, and this fact is better seen in grazing incidence angles of 4° and 6°, which indicate which exist more TiN in the film obtained in 120 minutes than the one obtained in 45 minutes in similar conditions. Therefore, it is evidence that there is an increasing in thickness for similar condition when the deposition process is longer.



(a) (b)

Figure 9. XRD pattern for TiN film obtained in different deposition conditions (a) in 0.5º grazing incidence angles and (b) in 6º grazing incidence angle

The figure 9 shows the comparison for the XRD pattern on 0.5º e 6º grazing incidence angle for the TiN films in different deposition conditions. Thus, the different peak intensity was more evident for the obtained samples in 33.3% N_2 – 44.4% Ar – H_2 gas mixture in 45 and 120 minutes. As the peak intensity is proportional to TiN phase amount on sample, it is possible to affirm that the increasing deposition time results in thicker film. When compared to the other deposition conditions, it is possible to notice differences in the peaks intensities and in its positions. However just in these results, it is not possible to affirm in which deposition conditions the obtained film was thicker.

4. CONCLUSIONS

It was obtained TiN films on glass surface using cathodic cage technique on different plasma atmosphere and different deposition times; therefore, it is proved that cathodic cage is an efficient technique for TiN film deposition. The deposition time influenced in film thickness, that is was proved through X-ray diffraction analysis for sample deposited under 33.3% N_2 – 44.4% Ar – H_2 gas mixture plasma in 45 minutes and 120 minutes. The sample deposited during more time had a thickness that was explained by TiN peaks more intensity. The active plasma species influenced the characteristics of TiN films, which could be seen through the comparison between OES spectra and X-ray diffraction pattern.

5. REFERENCES

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6. RESPONSIBILITY NOTICE

Natália de Freitas Daudt, Júlio César Pereira Barbosa, Leandro Augusto Pinheiro do Nascimento and Clodomiro Alves Junior are the only responsible for the printed material included in this paper.