Electrochemical Behavior of Titanium Nitride Thin Films Deposited on Silicon by Plasma Discharge Technique in Cathodic Cage

Cintia de Laet Ravani Bottoni[a]*, Mauro César Dias[b], L. C. Gontijo[a]

[a]*Postgraduation program in Metallurgical and Materials Engineering, Instituto Federal do Espírito Santo – IFES, Vitória, ES, Brazil*
[b]*Instituto Federal do Espírito Santo – IFES, Vitória, ES, Brazil*

Titanium nitride films were deposited on silicon by plasma discharge in cathodic cage with holes and without holes on the sides. Each film was deposited with a pressure of 253 Pa, treatment time of 2 h, and at diverse conditions of temperature and gas flow of N_2 and H_2. The electrochemical polarization and electrochemical impedance techniques were used to understand the effect on the electrochemical properties of these films in relation to the presence or absence of holes on the sides of the cathodic cage and to investigate the electrochemical behavior of the films formed, which presented as both capacitive and resistive for the conditionsanalyzed.

Keywords: *thin films, titanium nitride, cathodic cage, EIS, polarization*

1. Introduction

Among the diverse techniques of Physical Vapor Deposition (PVD), the deposition of thin films with cathodic cage discharge is prominent. It is based on sputtering and is one of the newest techniques of thin film deposition. The cathodic cage was developed and patented by the Laboratory for Plasma Processing of Materials of the Federal University of Rio Grande do Norte (UFRN) (PI0603213-3) to be initially used in the processes of plasma nitriding and recently started to be used for thin films deposition[1]. It consists of a cylinder with or without holes and a circular cover with similar holes (Figure 1)[1]. The experimental importance of this technique is that it eliminates the edge effect and overheating in nitriding processes, which occur during thermochemical treatment with plasma[2]. Furthermore, numerous advantages can be observed in the deposition processes, such as: use of equipment already presentin most plasma laboratories; high rate of films deposition; deposition of amorphous films with magnetic properties; possibility of deposition of films with resistivity compatible with semiconductors and dielectrics; films with excellent anodic properties, etc.

Thin films have great importance in high-tech industries, and the choice of titanium nitride as the material to be deposited is due to the range of technological applications that this ceramic material presents, such as: coatings for biomaterials[3]; coatings for cutting tools[4]; coatings for decorative pieces, and diffusive barrier in semiconductors[5].

Due to being widely used in coatings and to providing advantages– such as the use of the same system of conventional plasma nitriding, as already stated – this technique presents great potential for the deposition of films, since the films deposited through this technique present good resistance to corrosion and, in the case of titanium nitride, support very

high temperatures. Due to its use primarily as coating for cutting tools, we think that the evaluation of its electrochemical behavior – the aim of this article – is very timely since this technique is currently being developed.

Massiani et al. (1990) state that most studies on titanium nitride coatings are conducted on metal substrates and that the presence of surface defects on these materials contributes to electrochemical responses, especially during the time of immersion, as a result of the penetration of the electrolyte through the defects on the surface[6]. Initially, this paper proposed the use of an inert substrate (glass) to evaluate the electrochemical properties of thin films of titanium nitride without any contribution of an active substrate (metal): however, the results were still not satisfactory and this fact maybe can be explained by the very low electrical conductivity of these films and the difficulty in the preparation of electrodes for use in corrosion tests, hence silicon wafers were used, which is a semiconductor material and present better electrochemical behavior.

Considering the low cost of deposition, good appearance, different colors that these films have, and numerous applications that the films deposited through this technique present, this paper proposes to evaluate the electrochemical behavior of these films in a solution of 3.5% NaCl by mass using silicon wafers to evaluate the electrochemical properties of the thin films of titanium nitride.

2. Experimental Methods

2.1 Preparation and deposition of thin films

The materials used as substrate for deposition of films were silicon wafers with crystallographic orientation (100)

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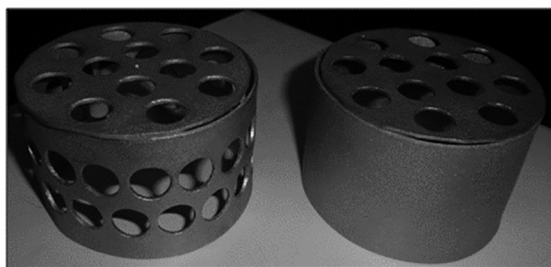Technique in Cathodic Cage

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Figure 1: Cathodic cages with holes and without holes on the sides.

– 10 mm wide, 25 mm long, and 2 mm thick. The two cages were made with grade II commercially pure titanium, both with 71 mm of diameter, 46 mm of height, and holes with 12 mm of diameter (for the covers and the cage with holes on the sides). The number of holes on the covers is the same for the two cages (12 holes), differing only in the number of holes on the side, as presented in Figure 1. Before each deposition procedure, the cathodic cages were chemically cleaned with a solution of 5% nitric acid (volume/volume) and 10% hydrofluoric acid (volume/volume).

The depositions were performed in a pulsed plasma nitriding reactor (SDS, Thor NP 5000) that consists of a cylindrical chamber 304 AISI stainless steel with 70 cm high and 50 cm diameter. The reactor has a vacuum system, an input system and control of the gas required for deposition, as well as two electrodes and high-voltage supply of 537 V and frequency of 4 kHz. The reactor used in the deposition of titanium nitride can be schematized as shown in Figure 2.

Each film was deposited with a pressure of 253 Pa, treatment time of 2 h and at diverse conditions of temperature and gas flow of N_2 and H_2, as presented in Table 1. The use of hydrogen gas in the deposition of thin films is the fact that this step up sputtering. Furthermore, hydrogen is also used in the heating step the sample until the treatment temperature was reached, and from this time, the nitrogen gas was added.

The films that were evaluated electrochemically are those from tests 1, 2, 3, 6, 8, and 9, under the conditions presented in Table 1, and the following codes were used to identify the samples:
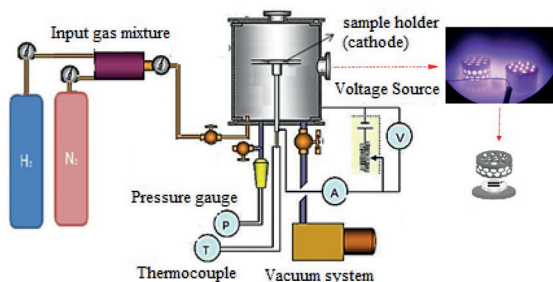

Figure 2: Reactor scheme used in the deposition of films.

Table 1: Maximum and minimum conditions for the variables: gas flow and temperature.

Nº of Test	Flow of N_2 (sccm)	Flow of H_2 (sccm)	T (°C)
1	72	128	365
2	178	22	365
3	72	128	435
4	178	22	435
5	50	150	400
6	200	0	400
7	125	75	350
8	125	75	450
9	125	75	400
10	125	75	400
11	125	75	400

- ENS.1:GSF, ENS.3:GSF, ENS.6:GSF,and ENS.9:GSF → films deposited under the test conditions 1, 3, 6,and 9, respectively, for the cage without holes on the sides; and
- ENS.1:GCF, ENS.2:GCFe ENS.8:GCF → films deposited under the test conditions 1, 2, and 8, respectively, for the cage with holes on the sides.

Seven samples were analyzed, in addition to the white one, which is the silicon substrate without deposition of film.

2.2 Electrochemical Techniques

The evaluation of the electrochemical behavior of the thin films was performed by means of polarization tests with open circuit potential and electrochemical impedance spectroscopy (EIS). The equipment used was a potentiostat Ivium CompactStat belonging to the Laboratory of Corrosion from Propemm/IFES, which was controlled by a computer at room temperature (23–25°C). The electrochemical cell used in the tests consisted of three electrodes: a reference electrode (calomel), the counter electrode (platinum), and the working electrode.

In the EIS, the stabilization of the equilibrium potential (OCP) was performed in a time of 30 minutes and, then, the test was initiated with a frequency range from $1x10^6$ to $4x10^3$ Hz and amplitude of $1x10^{-2}$ V, while the polarization test was performed with an initial scan potential of -0.4 V before the equilibrium potential and with final potential of 1.5 V with scan speed of 1 mV/s. The analyses of the EIS tests will be presented as Nyquist and Bode plots, while the polarization tests were presented in polarization curves using an aqueous solution of 3.5% NaCl by mass was used as an electrolyte.

3. Results and Discussions

Figure 3 shows the polarization curves for the samples of thin films deposited on silicon for the condition of test 1, both for the cage with hole (ENS.1:GCF) and for the cage without hole (ENS.1:GSF), and of test 6 for the cage without hole (ENS.6:GSF) and for white (silicon with no film deposited).
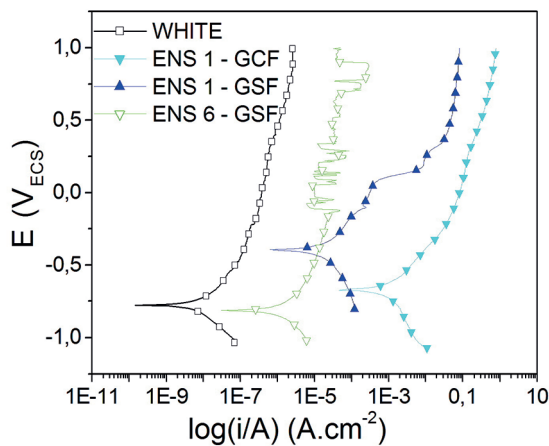

Figure 3: Polarization curves of the thin films of tests 1, 6, and white.

Considering the analysis of Figure 3, it is observed that among the curves of the films, the green graph (ENS.6:GSF) showed corrosion potential (-0.7 V) and current density closer to white, which is a sample of silicon with no film deposition. The corrosion potential of this sample differs slightly from the corrosion potential of white; however, the current density is two orders of magnitude greater than white. On the other hand, the dark blue graph (ENS.1:GSF) showed the most noble corrosion potential (-0.3 V) and a current density 3 orders of magnitude greater than white. According to Wolynec[7], the low current density and the high corrosion potential are desirable anodic characteristics in a material for this material to have a high resistance to corrosion. Therefore, it is observed that the white, despite not presenting the most noble corrosion potential, presents the best results in terms of current density. Among the films, it can be observed that the film ENS.1:GSF showed better results in terms of corrosion potential, and the film ENS.6:GSF was better in terms of current density. Despite the samples with deposited films presenting a greater current density than that of white, these values are quite satisfactory, since they are very close to the density values of white, which leads us to consider that these films have high resistance to corrosion. It is noteworthy that we are conducting our comparisons in relation to a semiconductor that is widely used in the market.

Figure 4 shows the Nyquist plots for the samples of tests: 1(GCF and GSF), 2(GCF), 3 (GSF), 6 (GSF), 8 (GCF), 9 (GSF), and white, in this order, obtained in a solution of
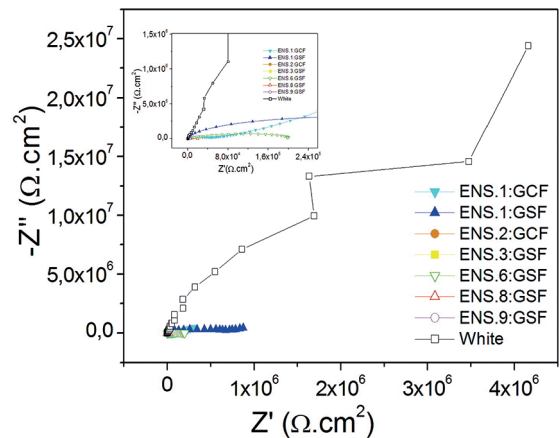

Figure 4: Nyquist plot obtained in chloride medium for the samples of tests 1 (GSF and GCF), 2 (GCF), 3 (GSF), 6 (GSF), 8 (GF), 9 (GSF),and white.

3.5% NaCl by mass. In these plots, it can be verified that the films have very distinct capacitive and resistive behaviors.

The films of ENS.2:GCF and ENS.3:GSF presented a highly resistive behavior, indicating that these materials have high resistance to the passage of current and present a very low charge storage capacity. The films of ENS.9:GSF, ENS.8:GCF,and ENS.6:GSF are also resistive, however in lower intensity if compared with the films of tests 2 and 3, while the samples ENS.1:GSF and ENS.1:GCF and white are more capacitive, i.e., they can store charges, although they also present resistive behavior, as shown in Figure 5.

By analyzing Figures 5(a) and 5(b), which represent the Bode plots of the phase angle versus logarithm of frequency and of the logarithm of impedance versus logarithm of frequency, respectively, it is observed that the films have some heterogeneity and present formation of other phases due to oscillations in a few films, such as the samplesENS.6:GSF (green)and ENS.1:GCF (blue fluorescent). The sample ENS.1:GSF presents as capacitive and resistive and indicates the presence of a constant phase element (Q), which is related to the homogeneity of this film. The samplesENS.2:GCF and ENS.3:GSF are highly resistive, since the graphs, in terms of phase angle, are close to zero angle, as well as those of ENS.8:GCFand ENS.9:GSF,which are also resistive. On the other hand, for the samples ENS.1:GCF and ENS.6:GSF,we can observe that their plots are characterized by a relatively flat capacitive arc in comparison to the other samples. This demonstrates that in the mid-frequency region there is less charge storage capacity, and that in the low-frequency region there was a possible detachment of the film from the substrate.

All these samples presented a decrease of the phase angle in the low-frequency region, which indicates a decrease in the capacitive behavior; however, the sample ENS.1:GCF presented behavior similar to the white, since both showed a large frequency range with a high phase angle, which demonstrates a high charge storage capacity,
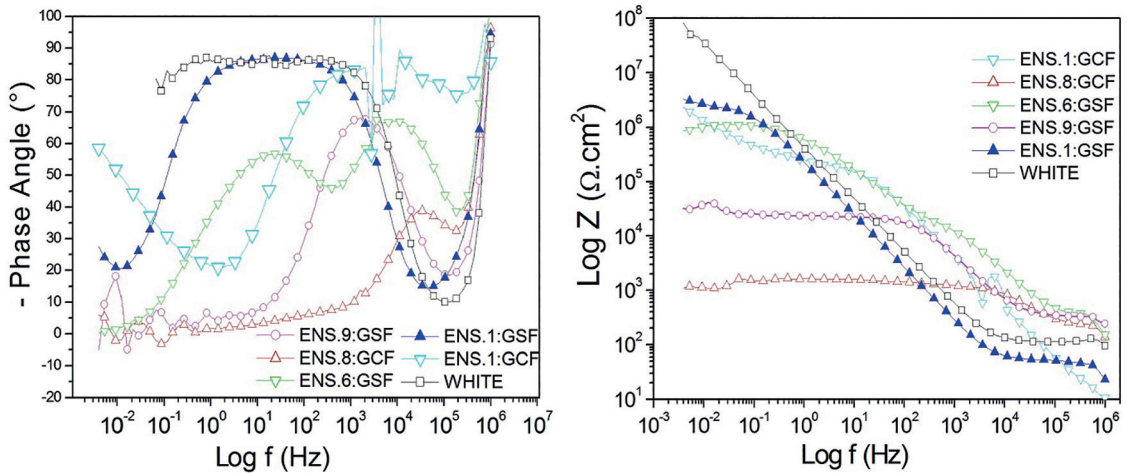
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Figure 5: (a) – Bode plot of the phase angle versus logarithm of frequency for the samples of tests 1 (GSF and GCF), 2 (GCF), 3(GSF), 6 (GSF), 8 (GCF), 9 (GSF),and white

therefore presenting high resistance to corrosion, although the sample ENS.1:GCF has also shown this decrease in the high-frequency region.

The analysis of Figure 4(b) enables the observation that the films of ENS.8:GCF and ENS.9:GSF presented the lowest values of Z in relation to white and, thus, have lower surface resistance to passage of current. It is also observed that the sample ENS.8:GCF has the lowest surface resistance of all the samples, while ENS.1:GSF has the highest surface resistance of all the other samples. These results demonstrate the capacity of the technique to deposit films with high resistance to corrosion. Additionally, it enables coating noble materials at low cost, making them high-performance materials.

4. Conclusions

In all the process conditions studied, it was possible to obtain thin films with highly varied anodic properties. This confirms the efficiency of the plasma deposition technique using cathodic cage. The configuration of the cages, the presence or absence of holes on the sides, the gas atmosphere, and the treatment temperature influence the deposition process and, hence, the properties of the thin films formed. These differences, especially in relation to the holes of the cage, influenced the electrochemical properties, because the films had both capacitive and resistive behavior for the conditions analyzed in these two cages. It is still necessary to know the range of possibilities of this technique. Therefore, further research is already being conducted based on this work and on those of Universidade Federal do Rio Grande do Norte (UFRN), which, to date, are the only ones in the literature on deposition of thin films by plasma using cathodic cage.

6. References

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