TiN thin film deposition by cathodic cage discharge: effect of cage configuration and active species

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Abstract. Plasma cathodic cage technique was developed recently in order to eliminate phenomena such as edge effects and overheating, which occur during conventional nitriding processes. In this work, the effect of plasma active species and cage configurations during thin film deposition of TiN were studied. This compound was chosen because its properties are very sensitive to slight variations in chemical composition and film thickness, becoming a good monitoring tool in fabrication process control. In order to verify the effect of cage geometry on the discharge and characteristics of the grown film, a cage made of titanium was used with different numbers and distribution of holes. Furthermore, different amounts of hydrogen were added to the Ar + N₂ plasma atmosphere. Flow rates of Ar and N₂ gas were fixed at 4 and 3 sccm, respectively and flow rates of H₂ gas was 0, 1 and 2 sccm. Plasma species, electrical discharge and physical characteristics of the grown film were analyzed by Optical Emission Spectroscopy (OES), Atomic Force Microscopy (AFM), X-Ray Diffraction. It was observed by OES that the luminous intensity associated to Hα species is not proportional to flow rate of H₂ gas. Electrical efficiency of the system, crystal structure and topography of the TiN film are strongly influenced by this behavior. For constant flow rate of H₂ gas, it was found that with more holes at the top of the cage, deposition rate, crystallinity and roughness are higher, if compared to cages with a small number of holes at the top of cage. On the other hand, the opposite behavior was observed when more holes were located at the sidewall of cage.

1. Introduction

Cathodic cage plasma technique was recently developed in order to eliminate edge effects and overheating, which occur during thermochemical treatment with plasma. These effects take place due to high superficial area/volume ratio, mainly in pieces with complex geometry [1-3].

The technique is used to protect electrically the workpiece during the process, resembling a Faraday cage device. An isolator is placed between the workpiece and the cathode, in order to keep the workpiece in a floating potential [4]. In this configuration, only the cage is in cathodic potential, producing a hollow cathode effect in each hole. Due to the higher density of ions formed in the holes of the cage; there is a higher sputtering rate in that region. The combinations of the gas species with the sputtered species present in plasma are directed towards the substrate surface, where they are...
deposited and diffused onto the sample [5]. Thus, it is possible to produce a hybrid process of deposition and diffusion, since the substrate temperature is high enough to promote diffusion.

Titanium nitride films are used in various industrial applications, for example, in metallurgical industry as coatings for high hardness and low friction [6] and in decorative coatings to replace gold, since different color tones may be achieved by variation of the Ti/N ratio [7]. The material is also used in optical applications as coatings of solar cells and solar control windows [8], in coatings of biocompatible alloys for biomaterials [9] and in coatings for microelectronic semiconductors [10]. Properties of titanium nitride films are very sensitive to small variations in chemical composition and thickness. Therefore, this sensibility is a useful tool to monitoring the fabrication process control.

Since this technique was developed recently, there are few studies about the influence of process parameters on the characteristics of the film grown. Therefore, this work proposes to investigate the efficiency of this technique to obtain TiN thin films. The effects of plasma active species and the influences of cage configuration on the deposition rate, on electrical parameters, on the microstructure and topography of the grown film on were investigated by Optical Emission Spectroscopy (OES), Atomic Force Microscopy (AFM) and X-Ray Diffraction.

2. Materials and Methods

Rectangular glass samples with 25 mm x 10 mm x 2 mm (length x width x thickness) were used in this work. The deposition was made using an ion nitriding reactor adapted to cathodic cage configuration. The samples were isolated of cathode by an alumina disk. The cages were made of commercially pure titanium (grade II) and have holes with 12 mm of diameter on the top and sidewall, covering all over the surface of the device. Figure 1 illustrates the reactor and a cage with its respective nomenclature.

Four different cages were used and denominated as L1T4, L1T8, L2T4 and L2T8. The L is referent to the number of lines of holes in the sidewall of cage and T is referent to the number of lines of holes on the top (covering) of the cage.

![Figure 1](image). Schematic representation of (a) plasma reactor and (b) cathodic cage with respective nomenclature for different cage configurations.

Ar and N₂ gas flow rates were fixed at 4sccm and 3 sccm, respectively and for H₂ were used gas flow rates of 0, 1 and 2 sccm. Argon was used to increase titanium sputtering rate and to control nitriding rate of the cage [11]. Hydrogen was used to reduce the presence of superficial oxides and to
increase process efficiency [12]. Pressure and temperature were fixed at 1.5 mbar and 450 °C, respectively. Table 1 shows the experimental conditions.

**Table 1.** Experimental conditions used in this work.

| Sample   | H₂ gas flow (sccm) | Pressure (mbar) | Current (A) | Voltage (V) | Power (W) | Number of holes | Cage height (mm) |
|----------|---------------------|-----------------|-------------|-------------|-----------|-----------------|------------------|
| L1T4     | 0                   | 1.45            | 0.30        | 877         | 263       | 16              | 8                | 34               |
| L1T8     | 0                   | 1.46            | 0.33        | 868         | 286       | 16              | 12               | 34               |
| L2T4     | 0                   | 1.47            | 0.35        | 846         | 296       | 31              | 8                | 45               |
| L2T8     | 0                   | 1.45            | 0.35        | 890         | 311       | 31              | 12               | 45               |
| L1T4-1   | 1                   | 1.48            | 0.30        | 860         | 258       | 16              | 8                | 34               |
| L1T8-1   | 1                   | 1.49            | 0.31        | 820         | 254       | 16              | 12               | 34               |
| L2T4-1   | 1                   | 1.48            | 0.33        | 811         | 267       | 31              | 8                | 45               |
| L2T8-1   | 1                   | 1.50            | 0.36        | 878         | 316       | 31              | 12               | 45               |
| L1T4-2   | 2                   | 1.51            | 0.32        | 808         | 258       | 16              | 8                | 34               |
| L1T8-2   | 2                   | 1.49            | 0.31        | 820         | 254       | 16              | 12               | 34               |
| L2T4-2   | 2                   | 1.52            | 0.35        | 817         | 286       | 31              | 8                | 45               |
| L2T8-2   | 2                   | 1.52            | 0.36        | 828         | 298       | 31              | 12               | 45               |

The deposition process was monitored by Optical Emission Spectroscopy (OES), using an Ocean Optics USB 4000 spectrograph. The X-Ray Diffraction analyses were performed with a Shimadzu XRD-6000 diffractometer using Cu radiation Kα and an accessory for Grazing Incidence X-ray Diffraction (GIXRD) and angle of incidence fixed at 0.5°. The samples were also analyzed by Atomic Force Microscopy (AFM) in contact mode with a Shimadzu microscope model SPM 9600.

3. Results and discussion

Figure 2a shows a typical OES spectrum obtained during cathodic cage deposition with the L1T8 configuration, where some lines corresponding to Ar, H₂, N₂ and N₂⁺ transitions are highlighted.
Figure 2. Plasma spectra obtained during deposition process in L1T8 configuration in different H\textsubscript{2} gas flow rates.

Figure 3. Species intensities for different configurations of plasma cage (bars) and values of the power supplied to keep the system at 450 °C (black dots).
Figure 3 shows the intensities lines relative to argon (750.3 nm) of N$_2$\textsuperscript{+}, N$_2$ and H$\alpha$, with respective emissions lines at 391.4 nm, 337 nm and 656.3 nm. The intensities of H$\alpha$ lines are not proportional to the H$_2$ gas flow rate used in this work as shown in the Figure 2. The line at 656.3 nm corresponding to H$\alpha$ has a maximal intensity at 1 sccm and it decreases in intensity when the gas flow rate is elevated to 2 sccm. Similar behavior is also observed for the other cage configurations (Figure 3). The intensities of N$_2$\textsuperscript{+} lines are not related to the H$_2$ gas flow rate. Emission depends more on cage configuration than on H$_2$ gas flow rate (figure 3).

Plasma efficiency in the heat transfer can be estimated by the ratio between the power supplied in the system (electric power) and the average of the species energy (line or band intensities). The results indicated that the optimal configurations were the L1T8 and L1T4 cages. A higher density of emitted species does not mean satisfactory energy efficiency to heat the cage, as can be observed in the configuration L2T4-2 (Figure 3), where the luminous intensity of species is maximal, but the power supplied to maintain the system at 450 °C is not the lowest one.

Figure 4 (a) shows the XRD patterns of deposited films with the L1T8 cage configuration using the different flow rates of H$_2$ gas (configuration that presented the highest TiN intensity). Moreover, Figure 4 (b) also shows a comparison between the XRD patterns of deposited films from L1T8 with the others cage configurations (all films deposited with 1 sccm flow rate of H$_2$ gas).

In general, the configuration with more holes at the covering exhibits higher efficiency. However, the highest efficiency was achieved when the lowest amount of holes is present at the sidewall. Apparently, this result is contradictory, since increasing the number of holes, it is expected that heating is promoted due to the increase in areas with hollow cathodes effect. This result is justified by the increase of the distance between the pieces and the top of the cage, when the number of holes in the sidewall is increased. Once that the heat from these holes is transferred to the chamber walls, to the inner and to the outer cage, there is an appropriate height at 34 mm which the maximum efficiency is promoted due to combination of heating by hollow cathode effect in covering and sidewall of cage.

![X-ray pattern with grazing incidence angle of 0.5 ° for films deposited with (a) the L1T8 cage configuration at different hydrogen flow rates and (b) different cage configurations at 1 sccm of H$_2$ gas flow rate.](image)
Microstructural characteristics of the grown films obtained by GIXRD shown an abrupt increase in TiN intensity and decrease in the full width at half-maximum (FWHM) when flow rate of H\textsubscript{2} gas is added (Figure 4a). It has been observed by other authors [13-16] that hydrogen reduces both superficial oxide formed spontaneously on the cage and titanium nitride formed on the inner walls of cage holes during plasma treatment, which causes surface poisoning. In this work, it was observed that H\textalpha species plays a key role in the deposition rate of TiN, because there is an increasing in deposition rate since there is a reduction in cage poising, promoting a formation of more stoichimonetry film.

The most intense TiN peak was observed with the cage configuration L1T8. On the other hand, the configuration L1T4 exhibited the lowest intense TiN peak due to low signal and high noise ratio. Furthermore, this configuration also produced lower luminous intensity associated to H\textalpha species at 1 sccm of H\textsubscript{2} gas flow rate, as can be seen in Figure 3.

![Figure 5](image)

Figure 5. Nanotopography of the TiN films surfaces deposited by L1T8 cage configuration at different flow rates of H\textsubscript{2} gas (a) 0 sccm, (b) 1 sccm and (c) 2 sccm.

| Cage configuration | Flow rate of H\textsubscript{2} gas (sccm) | \(I_{H\alpha}/I_{Ar}\) | Intensity \(\delta\)-TiN (200) | FWHM | Roughness |
|--------------------|------------------------------------------|-----------------|-------------------|------|-----------|
|                    |                                          |                 |                   |      | Ra        | Rms      |
| L1T8               | 0                                        | 30267           | 264               | 2.75 | 4.49      | 3.60     |
| L1T8               | 1                                        | 53643           | 5176              | 0.91 | 4.27      | 3.53     |
| L1T8               | 2                                        | 48337           | 3158              | 1.05 | 4.32      | 3.49     |
| L2T8               | 1                                        | 44900           | 2862              | 1.01 | 1.77      | 2.24     |
| L1T4               | 1                                        | 41989           | 1520              | 1.57 | 3.66      | 2.95     |

Table 2. Characteristics of the crystal structure and topography of films deposited at different H\textsubscript{2} gas flow rates and different cage configurations.

Table 2 shows \(I_{H\alpha}/I_{Ar}\) line intensity values obtained from OES spectra (Figure 3), FWHM values obtained from XRD patterns (Figure 4) and roughness values obtained from nanotopography (Figure 5). There is a correlation between the luminous intensity of H\textalpha species and the grown film characteristics. The higher deposition rate, (demonstrated by the intensity of TiN (200) diffraction peak) and higher crystallinity (demonstrated by the FWHM) occurred when the \(I_{H\alpha}/I_{Ar}\) ratio was higher. A relationship between roughness and H\textalpha intensity was found, since roughness increases when the luminous intensity of H\textalpha decreases. This effect occurred due to reduction of nitrogen and argon...
amount in plasma mixture, since nitrogen and argon have a higher atomic mass than hydrogen, they promote a higher sputtering rate in the grown film, resulting in a more roughness surface [11].

Furthermore it is possible to notice that the increase of the number of holes in the sidewall promotes a reduction of roughness. It is related to minor sputtering rate, since the increase of the distance between the pieces and the top of the cage decreases the probability of sputtered atoms collide with sample.

4. Conclusions

TiN films were obtained on glass substrates by cathodic cage discharge. It was found that deposition rates depend on the gas species density and cage configurations, which leads to obtain films with different roughness and microstructures.

Some conclusions can be made from these results:
1. The luminous intensity of the H α species is not directly dependent on flow rate of H 2 gas. There is maximum line intensity at 1 sccm flow rate of H 2 gas and line intensity decreases when flow rate of H 2 gas is increased to 2 sccm.
2. L1T8 and L1T4 cage configurations, in this order, are the most efficient when the ratio between supplied power and average energy of the species is considered.
3. In general, configurations with more holes at the top of the cage exhibit higher efficiency. However, this is not observed when the holes at sidewall of the cage are more numerous. Actually, in this case, the efficiency is lower.
4. There is a correlation between the luminous intensity of H α species and the characteristics of the grown film. Higher deposition rate and higher crystallinity were obtained with a higher $I_{H\alpha}/I_{Ar}$ ratio. Furthermore, there is a tendency of roughness increases when luminous intensity of H α increases.

References

[1] Sousa R R M, Araújo F O, Ribeiro K J B, Costa J A P, Sousa R S and Alves Jr. C 2008 Surface Engineering 24 313-318
[2] Sousa R R M, Araújo F O, Ribeiro K J B, Mendes M W D, Costa J A P and Alves Jr. C 2007 Materials Science and Engineering A 465 223-227
[3] Ribeiro K J B, Sousa R R M, Araújo F O, Brito R A, Barbosa J C P and Alves Jr. C 2008 Materials Science and Engineering A 479 142-147.
[4] Alves Jr. C, Araújo F O, Ribeiro K J B, Costa J A P, Sousa R R M and Sousa R S 2006 Surface and Coatings Technology 201 2450-2454.
[5] Gallo S C and Dong H 2010 Vacuum 84 321-325
[6] Peng Z, Miao H, Qi L, Yang S and Liu C 2003 Acta Materialia 51 3085-3094
[7] Roquiny Ph, Bodart F and Terwagne G 1999 Surface and Coatings Technology 116-119 278-283
[8] Smith G B, Ben-David A and Swift P D 2001 Renewable Energy 22 79-84
[9] Cheng Y and Zheng Y F 2006 Materials Science and Engineering A 434 99-104
[10] Wittmer M, Noser J R and Melchior H 1983 Journal of Applied Physical 54 1423-1428
[11] Sankar M B, Pal A R, Bailung H and Cuthia J 2008 Applied Surface Science 254 5760-5765
[12] Tamaki M, Tomii Y and Yamoto M 2000 Plasma and Ions 3 33-39
[13] Safi I 2000 Surface and Coating Technology 127 203-217
[14] Figueroa C A and Alvarez F 2006 Applied Surface Science 253 1806-1809
[15] Priest J M, Baldwin M J and Fewel M P 2001 Surface and Coatings Technology 145 152-163
[16] Sharma M K, Saikia B K, Phukan A and Ganguli B 2006 Surface and Coatings Technology 201 2407-2413