# Mechanical Properties of Ti-Si-N thin coating films produced by reactive magnetron sputtering

## Propiedades mecánicas de Recubrimientos de Ti-Si-N sintetizado por pulverización catódica reactiva

Received: 23 - 02 - 2015 Accepted: 25-05-2015

Jose Luis Guerra Betancourt[1]
Juan Manuel González Carmona[2]
Alexander Ruden Muñoz[3]
Carolina Ortega[4]
Federico Sequeda[5]

[1] Colombian. Materials Engineer. Research Group: Laboratory of Hard Coatings and Industrial Applications (RDAI, acronym in Spanish). Universidad del Valle, Cali, Colombia.
e-mail: guerrabetan@hotmail.com.
[2] Colombian. Ph.D. Research Group: Laboratory of Hard Coatings and Industrial Applications (RDAI, acronym in Spanish), Universidad del Valle, Cali, Colombia.
e-mail: juanmgonzalezc@gmail.com.
[3] Colombiano. Ph.D. Professor, Research Group: Laboratory of Hard Coatings and Industrial Applications (RDAI, acronym in Spanish), Faculty of Basic Sciences, Universidad Tecnológica de Pereira, Pereira, Colombia.
e-mail: arudenm@gmail.com.
[4] Colombian. MSc in Chemical Engineering. Research Group: Laboratory of Hard Coatings and Industrial Applications (RDAI, acronym in Spanish), School of Materials Engineering, Universidad del Valle, Cali, Colombia.
e-mail: carolinaortega35@gmail.com.
[5] Colombian. Ph.D. Professor, Research Group: Laboratory of Hard Coatings and Industrial Applications (RDAI, acronym in Spanish), Universidad del Valle, Cali, Colombia.
e-mail: fsequeda@univalle.edu.co.

## Abstract

Ti-Si-N coatings were deposited by DC reactive magnetron sputtering on stainless steel AISI 304 substrates varying the $N_2$ flow, in order to study the effect on the structural, mechanical and tribological properties. The coatings were deposited using a 99.999 % purity Ti-Si (90-10 at. %) target. Structural characterization was performed by X-ray diffraction (XRD), observing peaks corresponding to crystalline TiN. As there is no evidence of the formation of the Ti-Si-N , Ti-Si, Ti or Si free phases, it was determined that the compound consists of TiN crystal grains in an amorphous matrix of SiN. This result is supported by FTIR and EDS analysis. The mechanical properties were studied by nanoindentation, obtaining hardness values of approximately 23 GPa when low $N_2$ flows were used.

***Keywords**:* FTIR; nitrogen flow; mechanical properties; Ti-Si-N protective thin films; XRD.

## Introduction

Thin film coatings are widely used in industrial development to improve the surface properties of tools and machine parts, increasing their lifespan service. Using this type of treatment, it is possible to reduce the cost of maintenance and premature replacement by new parts (Kauffmann *et al.*, 2005). Through the deposition of coatings by Magnetron Sputtering D.C and R.F, it is possible to improve the material performance in manufacturing applications, obtaining high hardness, stable friction coefficients, and resistance to oxidation at high temperatures (Tung *et al.*, 2004). In the case of hard coatings, such as the Silicon Titanium Nitride (Ti-Si - N), hardness equal to or greater than 30GPa, makes it very useful in applications such as dice and cutting tools (Jiang *et* *al.,* 2004). This ternary system has properties influenced by the incorporation of Silicon in the Titanium Nitride structure (TiN), adding it at first to form stable oxides and prevent that the conventional TiN will be affected by an intolerant oxidation, stabilizing it thermally (Tung, *et al.,* 2004). Among the microstructural configurations of the Ti-Si-N system, it includes the formation of TiN nanocrystals embedded in a $Si_3N_4$ amorphous matrix (Xu *et al.,* 2007). Other types of microstructures may occur due to the formation of a solid interstitial solution or by substitution of titanium or nitrogen atoms in the TiN crystallite. However, the interstitial solution has a cohesive energy lower than the TiN structure, which means that there is no such solution under equilibrium conditions (Liu *et al.,* 2011). Silicon Titanium Nitride is a ceramic material which has excellent properties such as high hardness, high wear resistance and corrosion at high temperatures, as well as a high melting point. This material has been deposited by several techniques including Magnetron Sputtering DC and RF (Tung *et al.,* 2004; Vaz *et al.,* 2001), inductively coupled plasma (ICP) with the aid of the Reactive Cathodic Sputtering System *Assisted hybrid* PVD / CVD), which combines the *Magnetron Sputtering* technique with plasma-induced gas-phase chemical processes (Zhang, 2003), which obtained very good results as high hardness and stable coefficient of friction, among other properties (Tung *et al.,* 2004). Due to these differences in composition and structure, tribological behavior and corrosion resistance will depend on these relationshipps; On the other hand, the high mechanical performances, the fragility, and the adhesion placed the Ti-Si-N as an abrasive material, with the influence of the particles that can be formed at the interface when tribological contact occurs, which undergo hardening processes by plastic deformation (Holmberg, and Matthews, 2009). Due to these difficulties, it is important to study these properties in terms of standardization of the procurement processes and their possible application. The present work will show the structural and mechanical study of Ti-Si-N coatings deposited on AISI 304 steel and synthesized by the *Magnetron Sputtering* Reactive technique.

## Methodology

Ti-Si - N coatings were deposited through the technique of PVD Magnetron Sputtering reactive nitrogen and argon environment by varying the $N_2$ flow using a reactor AJA International ATC 1500, on substrates of AISI 304 steel and glass, from a target predecessor of the Ti-10Si. The substrates were subjected to ultrasonic cleaning in an acetone environment for 15 minutes, in addition to surface cleaning with a pre-sputtering process in a controlled atmosphere of argon. The synthesis conditions of the coatings are shown in Table 1.

**Table 1.** Synthesis conditions of Ti-Si-N coatings

| Working Pressure (Wp) | Target Power Density ($W/cm^2$) | Polarization Voltage RF (V) | Flow ($Ar/N_2$) (s.c.c.m) | Substrate Temperature | Synthesis time (min) |
|---|---|---|---|---|---|
| $3x10^{-3}$ | 5 | -100 | 10/0.0<br>10/0.2<br>10/0.4<br>10/0.6<br>10/0.8<br>10/1.0 | TA* | 90 |

TA*: Ambient Temperature
**Source:**The authors

The chemical characterization of the coatings was carried out by means of Infrared Spectroscopy (FTIR) in a Jasco Spectra Manager FT / IR-4100 equipment, with a 45 ° Michelson Interferometer, cube type mirrors, with auto-alignment mechanism; Mechanical moving mirror drive with electromagnetic propulsion and digital control system; Opening diameter: from 0.5 mm to 7.1 mm in 8 steps; Beam splitter: KBr substrate coated with germanium. The FTIR spectra were recorded at 25 °C in the absorbance mode, in the frequency range of 400 to 4000 $cm^{-1}$. The crystalline structure was studied by X-ray diffraction (XRD) in a Bruker D8 ADVANCE unit with the copper source, Cu (λ = 1.5406 Å), under the grating beam diffraction method, an angle of incidence of 1 °, Sweeping angle 2θ between 20 °- 80 ° y de 0.02 per step. For the study of the mechanical properties, a NANOVEA module IBIS - Technology was used, using the method of Oliver and Parr (Oliver *et al.,* 2004), to adjust the charge - discharge curve. Nanoindentations were performed in the ranges: low (L), medium (M) and high (H); loads (B: 0.01-0.4mN, M: 0.41-1 mN and A: 1.1-10 mN); profiles of hardness and modulus of elasticity were obtained as a function of depth, which determined an ideal load of 1mN, which is below 10 % of the thickness for the coatings and eliminated the effects of the steel substrate.

The nanoindentation tests were performed using a Berkovich pyramidal indenter coupled to Fischer-Cripps Labs' IBIS Nanoindentation head and a displacement control frame with a compliance of 0.00035 µm/mN, IBIS SOFTWARE was used for control of Indentation, correction, and analysis of the result.

## Results

### *Structural analysis FTIR*

By means of the FTIR chemical analysis, the deposited coatings were characterized to determine the compounds present in the different samples through their vibrational modes (Skoog *et al.,* 2001). Figure 1 shows the spectra for the glass sample and the coatings deposited to flows of $N_2$ of 0.2, 0.6 and 1.0 SCCM. Glass was used as a substrate because this material does not present vibrations that can be overlaid with the elements and compounds under study (Skoog *et al.,* 2001). It is observed that there is no presence of vibration modes for coatings, which indicates that the deposited material does not generate radiation absorbance in the middle infrared zone. The Ti-Si or free titanium alloy (Mawhinney *et al.,* 1997; Llano *et al.,* 2007) shows that these elements or compounds are not present in the material because they do not find silicon vibration peaks, these do present radiation absorption in the middle infrared (Orduña et al., 2010; Mazaj *et al.,* 2009).

### *Structural analysis XRD*

Figure 2 shows the diffraction patterns for the coatings obtained. The characteristic peaks of the crystalline phase of TiN with face-centered cubic structure (FCC) are observed, with peaks in the crystallographic directions (111), (200), (220) and (311), with angles 2θ of approximately 36,42 °, 41,45 °, 59,08 ° and 70,53 ° degrees respectively. This type of network has the largest packing factor among all cubic cells showing better mechanical properties thanks to its crystallographic orientation (Pierson, 1996). The obtained patterns have an angular offset to the left compared to the spectra found in the literature (García-González *et al.,* 2006; Xu *et al.,* 2007), due to the existence of compressive residual stresses in the structure, Varying the network parameter (*Minigolo, 2001*). There was no evidence of the existence of free silicon, Ti-Si compounds and silicon nitride in the structure.

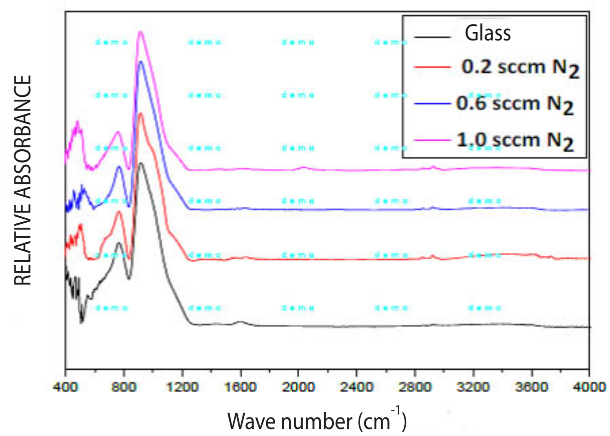


**Figure 1.** FTIR spectra for TiSiN hard coatings deposited on glass substrates. **Source:** The authors

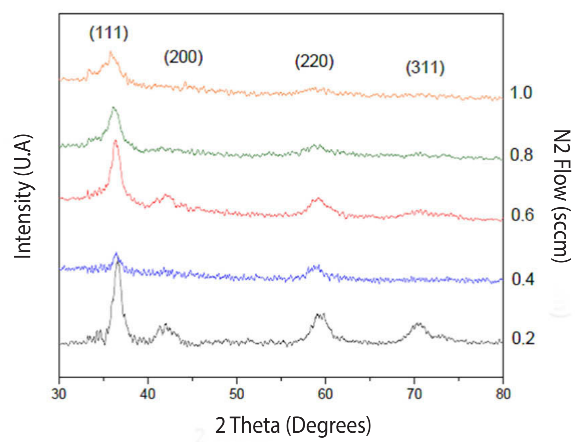


**Figure 2.** XRD pattern for Ti-Si-N hard coatings synthesized by Magnetron Sputtering. **Source:** The authors

Complementary to the FTIR analysis and looking the increase in the width of the peaks in the diffraction patterns, the experimental results indicate that the silicon nitride phases are presented in an amorphous form and the free silicon formation is discarded in the structure. This same aspect can be verified through the intensities ratio in the patterns, which clearly shows a reduction with respect to the width of the peaks as the $N_2$ flow is increased. In general, it is observed that by increasing the nitrogen flow there is a tendency for a crystallographic reorientation, due to the segregation of the silicon nitride amorphous phase, which suppresses the growth of TiN crystallites (Xu *et al.*, 2007). The diffraction pattern of the sample deposited with flow 0.2 sccm (standard cubic centimeters per minute) of nitrogen shows a higher ratio of intensities of the diffraction peaks, indicating a larger size of TiN crystallites. This crystallographic distribution has a greater orientation in relation to the other spectra obtained (Pierson, 1996). For the pattern of layers deposited with 0.4 sccm $N_2$, the intensity of the peaks (111) and (220) decrease and disappear the peaks associated with the crystallographic directions (200) and (311). This is attributed to the phenomenon of preferential crystallographic reorientation, due to the segregation of the silicon nitride amorphous phase (Xu *et al.*, 2007). The pattern of coatings deposited with 0.6 sccm of nitrogen is similar to the pattern of layers deposited with 0.2 sccm, indicating that a large amount of nitrogen has reacted, again forming the guidelines lost in the diffractogram of 0.4 Sccm, due to the stability of the TiN compound. The increase of nitrogen flow between 0.8 sccm and 1.0 sccm of $N_2$ shows a crystallographic reorientation, with a gradual spreading of the peaks, indicating the formation of smaller crystallites (Xu *et al.*, 2007; Míngolo, 2001). Previously performed work shows a similar behavior, indicating the effect of the nitrogen flow variation on the growth of Ti-Si-N coatings (García-González *et al.*, 2006). In addition, the amorphization that occurs in the compound has been studied as the result of segregation of the silicon nitride phase in the structure, finding an absence of titanium and / or free silicon, as well as the Ti-Si alloy (García-González *et al.*, 2006; Xu *et al.*, 2007). In order to confirm the presence of Si, surface EDS analysis was performed (Table 2), which shows percentages of silicon around 8% at.

**Table 2.** The Atomic percentage of Ti, Si and N elements on the surface of the coating.

| Flow of $N_2$ (sccm) | Ti (at%) | Si (at%) | N (at%) |
|---|---|---|---|
| 0.2 | 43.47 | 7.61 | 48.82 |
| 0.6 | 38.46 | 8.01 | 53.52 |
| 1.0 | 36.92 | 8.89 | 54.18 |

**Source:** The authors

The EDS analysis shows the elements that are on the surface of the coatings. Using XRD and FTIR analysis shows that the coatings do not have free elements in its structure either crystalline nor amorphous form, as well as the Ti-Si compound. This indicates that the only compounds present in the structure are Titanium Nitride (crystalline), due to the appearance of peaks in the diffractograms and Silicon nitride (amorphous).

## Study of mechanical properties

Table 3 shows the values obtained from indentation depth, with its deviation, and the resistance to plastic deformation; and Figures 3 and 4 show the hardness and elasticity modulus respectively for Ti-Si-N coatings deposited with different nitrogen flows. The hardness of the coating with 0.0 sccm $N_2$ flow is the lowest, because it is mostly composed of metallic material (Ti) (Kim *et al.*, 2003), unlike the coatings with some amount of nitrogen in its structure, which show a higher hardness compared with the Ti-Si coating (Figure 3). It is observed that the coating with flow 0.2 sccm $N_2$ possesses the highest hardness compared to the other coatings, because it presents the best intensities ratio in the peaks of the diffraction pattern, indicating greater crystalline coherence, larger sizes of Crystallite and densification of the coating (Pierson, 1996). In samples deposited with higher nitrogen flows, a slight variation of average hardness is observed, between 18 and 20 GPa.

**Table 3.** Measurements of mechanical properties for Ti-Si-N

| Flow $N_2$ (sccm) | H (GPa) | E (GPa) | Depth (nm) | Depth Deviation (nm) |
|---|---|---|---|---|
| **Steel** | 5.640 | 243.480 | ___ | ___ |
| 0.0 | 7.181 | 189.647 | 159.535 | 2.290 |
| 0.2 | 23.360 | 253.648 | 120.067 | 4.003 |
| 0.4 | 18.199 | 276.717 | 113.011 | 3.199 |
| 0.6 | 20.302 | 245.701 | 107.087 | 4.483 |
| 0.8 | 20.444 | 214.215 | 109.110 | 2.671 |
| 1.0 | 18.12 | 197.683 | 119.868 | 4.971 |

**Source:** The authors

This type of materials show high hardness compared to other coatings like TiN, due to the silicon promotes the segregation of the $Si_3N_4$ phase, which generates a strengthening similar to the conventional TiN (Tung *et al.*, 2004). In Figure 4 it is observed that the average elasticity modulus presents an increase to average nitrogen flows (from 0.2 sccm to 0.4 sccm) and decreases as it is increased. The obtained results indicate that the ceramic material has a better elastic recovery. For ceramic coatings the modulus shows a slight decrease with respect to the nitrogen flow; the largest modulus of elasticity is for the coating with flow 0.4 sccm $N_2$. The coating deposited with 0.0 sccm $N_2$ has the smallest elasticity modulus, due to the influence of the metallic material of titanium in its structure, which has greater plasticity compared with the ceramic coatings obtained.

Figure 5a and 5b show the charge-discharge curves for the Ti-Si coatings deposited to 0.0 and Ti-Si-N 0.2 sccm $N_2$, respectively. Figure 5a shows that Ti-Si material, influenced by the titanium in its composition, recovers elastically to a lesser extent when performing the discharge of the indenter, compared to the ceramic coatings. Figure 5b shows that the ceramic coating has a better elastic recovery since it shows a greater leftward shift of the curve in the discharge part of the indenter (Gómez, 2005). By means of the relation between hardness and elasticity modulus ($H^3/E^2$), the predominant mode of initial contact of the materials (Table 3) can be estimated by studying the plasticity index (Holmberg y Matthews, 2009). The analysis indicates that the coatings have a predominantly plastic initial contact, which increases the actual contact area; the highest values are the coatings deposited to flows of 0.0 sccm and 0.4 sccm $N_2$. Materials that have a predominantly plastic behavior, to be subjected to a load contact, the elastic limit is exceeded by leaving a permanent mark on the material, which is similar to that made to maximum indentation depth with the maximum load applied (Gómez, 2005). Due to the influence of the plastic behavior of the materials to be indented, the area of discharge obtained in the typical graphs of the hardness tests shows a smaller shift to the left, which means a less elastic recovery of the material (Gómez, 2005).

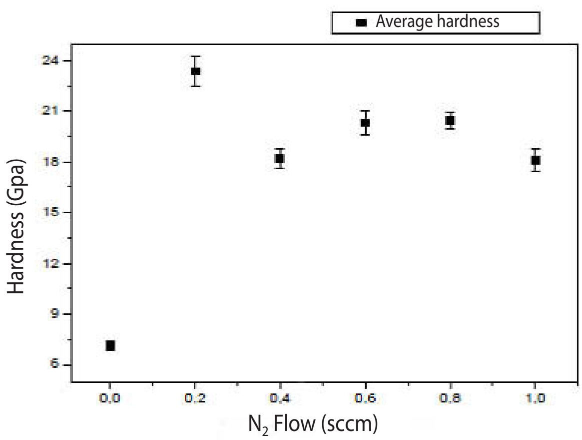


**Figure 3.** The Average hardness of Ti-Si-N coatings deposited to the different nitrogen flows.
**Source:** The authors

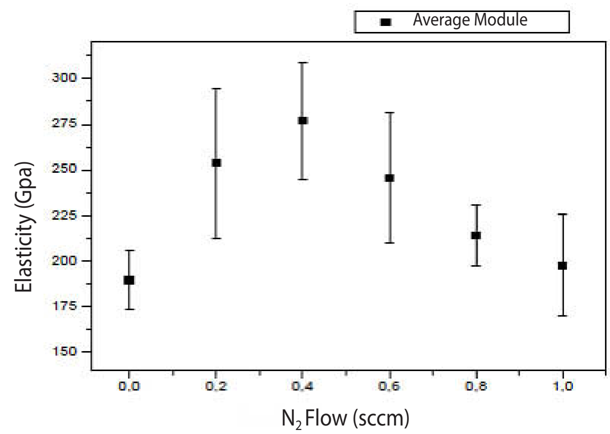


**Figure 4.** Elasticity modulus of the Ti-Si-N coatings deposited to the different nitrogen flows.
**Source:** The authors

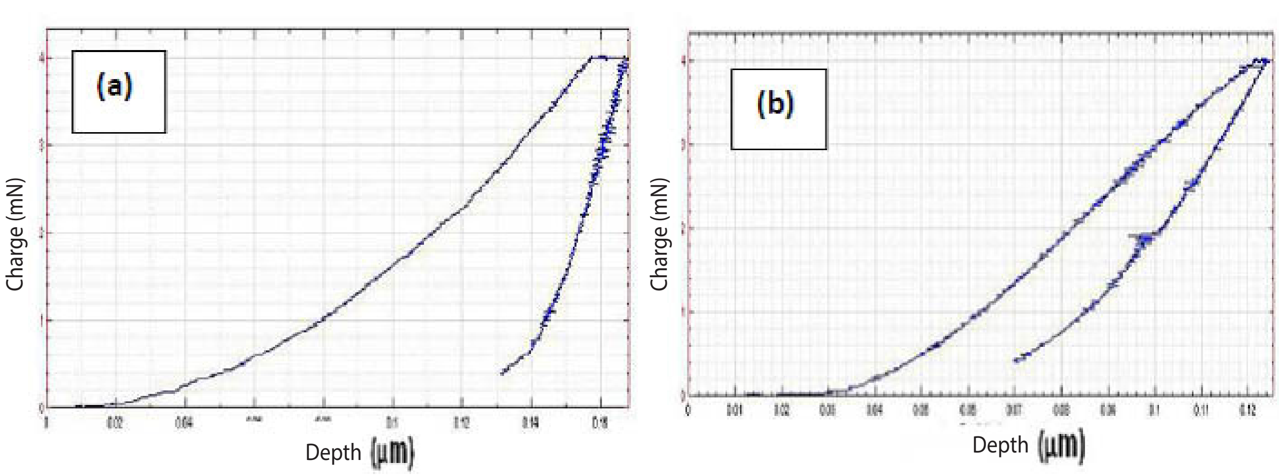


**Figure 5.** Charge- Discharge curves for Ti-Si-N coatings.
**Source:** The authors

## Conclusions

On the basis of the diffraction patterns, characteristic peaks of the crystalline TiN phase, with face-centered cubic structure (FCC), described by the crystallographic directions (111), (200), (220) and (311) were found, which present an angular offset to the left, indicating the existence of compressive residual stresses in the structure. By means of the FTIR analysis, no vibration modes were observed for the free elements or the alloy corresponding to the cathode, indicating that the material present is composed of the TiN crystalline phase, in an amorphous silicon nitride matrix. Ti-Si-N coatings have a high hardness; low nitrogen flows in the deposition were found hardness values around 23 GPa.

## Appreciation

The authors are grateful to the Universidad del Valle for the financing of the project titled: “Evaluation of the tribological behavior of intelligent self-lubricating coatings applied to steels used in pressure cams and hydraulic systems for industrial use” filing code: 2803.

## References

García-González, L.; Morales-Hernández, J.; Espinoza-Beltrán, F.J.; Muñoz-Saldaña, J.; Scholz, T.; Schneider, G.A. (2006). Thermal stability, structure and mechanical properties of TiSiN coatings prepared by reactive DC magnetron co-sputtering. *Materials Science Forum* 509, 93-98.

Gómez, M.A. (2005). *Caracterización de las propiedades tribológicas de los recubrimientos duros.* Memoria doctoral. Barcelona: Universidad de Barcelona. Departamento de física aplicada y óptica, pp. 14, 31-46, 51, 56-58, 201-204.

Holmberg, K.; Matthews, A. (2009). *Coatings Tribology: Properties, mechanisms, techniques, and applications in Surface Engineering*. Elsevier pp. 47-48, 103-104, 337-339, 320-336.

Jiang, N; Shen, Y.G; Mai, Y.-W; Chan, T; Tung S.C. (2004). Nanocomposite Ti–Si–N films deposited by reactive unbalanced magnetron sputtering at room temperature. *Materials Science and Engineering* B106, 163–171.

Kauffmann, F; Dehm, G; Schier, V; Schattke, A; Beck, T; Lang, S; Arzt, E. (2005). Microstructural size effects on the hardness of nanocrystalline TiN/amorphous-SiNx coatings prepared by magnetron sputtering. *Thin Solid Films* 473: 114–122.

Kim, G.S; Lee, S.Y; Hahn, J.H; Lee, B.Y; Han, J.G; Lee, J.H; Lee, S.Y. (2003). Effects of the thickness of Ti buffer layer on the mechanical properties of TiN coatings. *Surface and Coatings. Technology* 171, 83–90.

Liu, X.; Ren, Y.; Tan, X.; Sun, S.; Westkaemper, E. (2011). The structure of Ti–Si–N superhard nanocomposite coatings: ab initio study. *Thin Solid Films* 520, 876-880.

Llano, Bibiana; Marín, Juan Miguel; Restrepo, Gloria; Ríos Luis Alberto. (2007). Síntesis, caracterización y evaluación fotocatalítica de óxidos mixtos titanio-silicio. *Scientia et Technica* Año XIII, (36): 319-324.

Mawhinney, D; Glass, Jr., John A.; And. Yates, John T Jr. (1997). Ftir Study of the Oxidation of Porous Silicon. *J. Phys. Chem.* B 10: 1202-1206.

Mazaj, M; Stevens, W; Zabukovec Logar, N; Ristic A; Novak Tušar, N; Arcon, I; Daneu, N; Meynen, V; Cool, P; Vansant, E; Kaucic, V. (2009). Synthesis and structural investigations on aluminium-free Ti-Beta/SBA-15 composite. Microporous and Mesoporous. *Materials* 117, 458–465 .

Míngolo, N. y Ortiz, M. (2001). *Caracterización de recubrimientos y superficies por difracción de rayos X. Procesamiento de materiales por plasma*. Curso latinoamericano 4, 251-259.

Oliver, W.C; Pharr, G.M. (2004). Measurement of hardnessandelasticmodulusbyinstrumented indentation: Advances in understanding and refinements to methodology. *Journal of Materials Research* 19 (1), 3-12.

Orduña Díaz, A; Treviño Palacios, C.G; Rojas López, M; Delgado Macuil, R; Gayou, V.L;

Torres Jacome, A. (2010). Ftir and electrical characterization of a-Si:H layers deposited by PECVD at different boron ratios. *Materials Science and Engineering* B 174, 93–96.

Pierson, H.0. (1996). Handbook of refractory carbides and nitrides: Properties, characteristics, processing, and applications. *Noyes publications* 193, 219-221.

Skoog, D.A; Holler, F.J; Nieman, T.A. (2001). *Espectrometría de absorción en el infrarrojo. Principios de análisis instrumental*, pp. 411.

Tung, S.C; Yiang, N; Shen, Y.G; Li, L; Mai, Y-W; Chan, T. (2004). *Tribological characteristics of tisin films deposited by unbalanced magnetron sputtering*. Transient process in tribology Elsevier B.V, pp. 673-687.

Vaz, F; Rebouta, L; Goudeau, Ph; Girardeau, T; Pacaud, J; Rivie´Re, J.P; Traverse, A. (2001). Structural transitions in hard Si-based TiN coatings: the effect of bias voltage and temperature. *Surface and Coatings Technology* 146 –147, 274–279 .

Xu, Y; Li, L; Cai, X; Chu, P.K. (2007). Hard nanocomposite Ti–Si–N films prepared by DC reactive magnetron sputtering using Ti–Si mosaic target. *Surface and Coatings Technology* 201, 6824–6827.

Zhang, X. (2003). *Structure and mechanical properties of Ti-Si-N coatings.* Tesis maestria de ciencias en ingeniería mecánica. Louisiana, USA: Louisiana State University and Agricultural and Mechanical College. The Department of Mechanical Engineering.