

# XANES and EXAFS study of the TiN Thin films grown by the pulsed DC sputtering technique assisted by balanced magnetron

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Recibido el 2 de marzo de 2006; aceptado el 18 de agosto de 2006

A series of different  $Ti_xN_y$  thin films were grown by the DC-sputtering technique. The purpose for this work was to study through XAS interpretation, how the different amounts of  $N_2$  during growing thin TiN thin films, affects the stoichiometry of the TiN deposited. Also the results obtained determinate how to interpret the spectra to see the different valences of Ti in TiN, are working. The results were supported with the EXAFS and XANES analysis. This work concludes the adequated conditions for this experiment to obtain TiN as thin film by the DC sputtering assisted by pulsed balanced magnetron at room temperature and aconcludes which XANES spectra are the finger print for valences of Ti.

**Keywords:** TiN; Nitration; thin films; PLD.

Se creció una serie de películas delgadas de  $Ti_xN_y$  mediante la técnica de DC sputtering asistido por magnetrón balanceado en modo pulsado. El propósito del trabajo fue el de estudiar, mediante la interpretación de XAS, como las diferentes cantidades de nitrógeno suministrado durante el crecimiento de las películas delgadas de TiN, afecta la estequiometría del TiN depositado. También los resultados obtenidos determinan como se interpretan los espectros para observar las diferentes valencias del Ti en el TiN. Los resultados fueron obtenidos mediante el análisis XANES y EXAFS. Este trabajo concluye las condiciones adecuadas para este experimento y obtener TiN como película delgada mediante DC sputtering asistido por magnetrón balanceado en modo pulsado a temperatura ambiente y establece cual de de los espectros de XANES es la huella digital de las valencias de TiN.

**Descriptores:** Películas delgadas; TiN; nitruración.

PACS: 82.80.Dx; 68.55.-a; 81.15.Aa

## 1. Introduction

Hard coatings and their applications continuously are in progress. The thin films of transition metal nitrides have a broad range of potential applications that goes from micro-electronics to the metal-mechanics industry or in biological implants. The research of TiN is still on in actuality for the different science branches like the above mentioned.

Different techniques are used to growth thin films. Mostly used are RF [1-3] and DC-sputtering [4-16]. But these, requires about 500° C of temperatures for growing high purity TiN. Therefore there is a very interest in methods for growing TiN at low temperatures or room temperatures. So the pulsed balanced DC sputtering is very new established technique for growing thin films at room temperature [17-20].

A characteristic of this technique is that very slightly variations of the deposition parameters (target current and power, substrate temperature, partial pressure of a gas environment) result in a great alteration of the film properties. And as shown in this work, slightly variations of  $N_2$  atmosphere during the ablation of titanium, results in different  $Ti_xN_y$  thin films.

The results are accomplished by *ex-situ* analysis techniques, such as X-ray Absorption Near Edge Spectroscopy, (XANES) and Extended X-ray Absorption Fine Structure

(EXAFS). The EXAFS fit was done by using the FEFF 8.0 software in order to obtain the coordination number and the radial distance on each one.

## 2. Experimental details

### 2.1. Film preparation

All the thin films were deposited at room temperature in a Intercovamex V3 DC-sputtering system assisted by balanced magnetron in the pulsed mode, Deposition was performed by sputtering a 99.99% titanium target into an environment of high-purity molecular nitrogen. Nitrogen partial pressures  $P_N$ , were 5, 25, 30 and 50 mTorr. Layers were deposited on Si (111) *n*-doped silicon wafers without any pre-cleaning process. The base pressure in the growth chamber was maintained in the  $10^{-3}$  Torr.

Ti target was sputtered during 1 hour by using a pulsed 3" magnetron with a nominal power, during the evaporation, of 500W. The substrate was remaining at room temperature [21].

### 2.2. Film characterization

XAS experiments were carried out in the SSRL (Stanford Synchrotron Radiation Laboratory) beam line 7-3 assisted

by a Lytle detector by measuring the fluorescence emission. A singular problem appears when the resonance of the Si diffraction lines are overlapped into the XAS spectra, however these diffraction peaks are easily removed by deglitching the spectra in the Win XAS software. Typical runs were about 1 hour collecting absorption data around the Ti-L<sub>23</sub> edge located at energy of 4.5 KeV.

The valence of the Ti was obtained by comparing the edge of the samples. This analysis is knowledge as XANES analysis. The comparison was performed respect to TiO<sub>2</sub> foil.

EXAFS procedure was applied only to the Ti ionization edge by using the phase transferability principle [22].

### 3. Results and discussion

Figure 1 shows the XAS spectra around the Ti L<sub>23</sub> ionization edge after background subtraction. The pre-edge background was removed by the standard method of using a power-law function to curve-fit the pre-edge region and subtracting this function beyond the edge. The reduction in the oscillatory part from the L edge in EXAFS to the final form  $FT[\chi(k)k^2]$  involves, first, isolation of the L<sub>23</sub> edge contribution to the XAS function and, second, weighting of the extracted  $\chi(k)$  by a factor that adjust for the relatively stronger decay of the EXAFS amplitude. The fine structure range is marked with an arrow. In this case it was possible to establish the nature of the Ti binding by analyzing the near edge structure since the inelastic cross section for the L line due to the good resolution in the edge shapes.

The radial distribution function may be obtained by applying a fast Fourier transform, FFT to the background subtracted, k-converted extended fine structure. In the EXAFS case, the oscillations above the absorption edge are given by the equation:

$$\Phi_j(k) = \tan^{-1} \frac{\text{Re}[FFT^{-1}]}{\text{Im}[FFT^{-1}]} - 2kR_j \quad (1)$$

where  $\chi(k)$  is the oscillatory part,  $\vec{\varepsilon}_q \cdot \vec{r}$  is the dipolar term associated with the polarization of the x-rays and  $\psi_i, \psi_j$  the respective initial and final states of the electron. Applying an FFT to this oscillatory function a radial function (real space function) is obtained as follows:

$$F(r) = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} \chi(k) k^\mu \omega(k) e^{-2ik \cdot r} dk \quad (2)$$

Here  $k$  is the wave vector,  $k^\mu k$  is a weight factor to avoid any divergences in the integral where  $\mu$  may take values of 1, 2 or 3. The term  $\omega(k)$  is a selected window function and  $r$  is the respective radial distance.

In EXAFS, the main peaks in the radial distribution function do not correspond directly to the atomic positions on account of ionization and backscattering phase shifts [18]. The values for phase shifts for different edges, elements and backscatter have been tabulated [23-25]. However the phase

shifts can also be deduced directly using experimental data from a model compound of known structure. The experimental phase shifts can be used afterward in all compounds where the same absorber and backscatter pair is involved, invoking the phase shift transferability principle. In this case the experimental phase shifts can be obtained by using the Eq. (3), applied to experimental data of a sample of known structure. In this equation the quantities of  $\text{Re}\{FFT^{-1}\}$  and  $\text{Im}\{FFT^{-1}\}$  are the real part of the Fourier transform and the imaginary part of the inverse Fourier transform, respectively,  $\Phi_j(k)$  the respective experimental phase shifts,  $k$  the wave vector and  $R_j$  the atomic position of the  $j$  atom.

$$\Phi_j(k) = \tan^{-1} \frac{\text{Re}[FFT^{-1}]}{\text{Im}[FFT^{-1}]} - 2kR_j \quad (3)$$

The  $E$ -space XANES appears in Fig. 2. In this figure we can appreciate the difference among them, mainly in the TiN grown at 25 mTorr, were the small peak corresponding to the Ti<sup>2</sup> is practically negligible. Figure 3 shows the Fourier Transform obtained by applying the transformation described by Eq. 2. In this figure the first main peak of the TiN growth at 25 mTorr is located at 0.21 nm and the second main peak

TABLE I. Numerical results for the  $R$ ,  $N$ ,  $\Delta E_0$  and  $\Delta\sigma^2$  obtained by using the FEFF fit.

Sample	Radial distance for the first nearest neighbors (nm)	Radial distance for the second nearest neighbors (nm)	$\sigma^2$	Coordination number
5mTorr	0.180	0.285	0.0025	8.20
25mTorr	0.210	0.299	0.0056	0.25
30mTorr	0.175	0.290	0.5622	5.12
50mTorr	0.185	0.285	0.0252	5.01

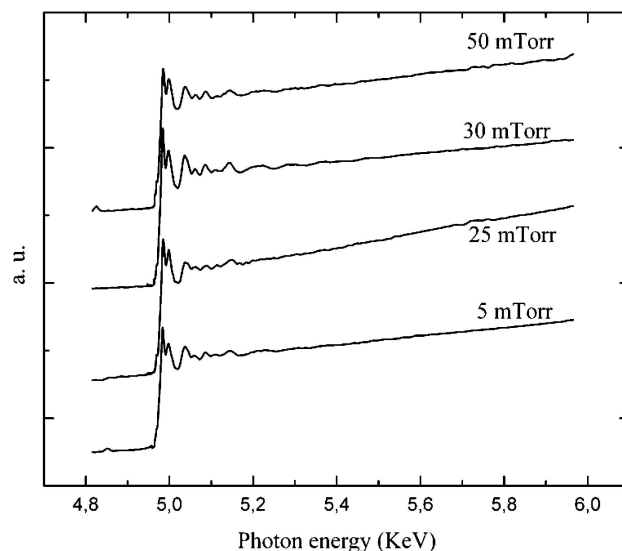


FIGURE 1. XAS spectra for the TiN samples around the TiL<sub>23</sub> ionization edge .

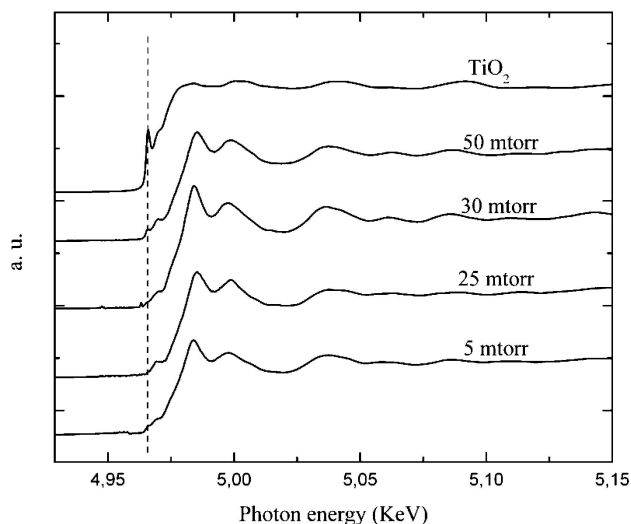


FIGURE 2. XANES spectra of the TiN samples. As we can see the difference in the TiN valence is well defined.

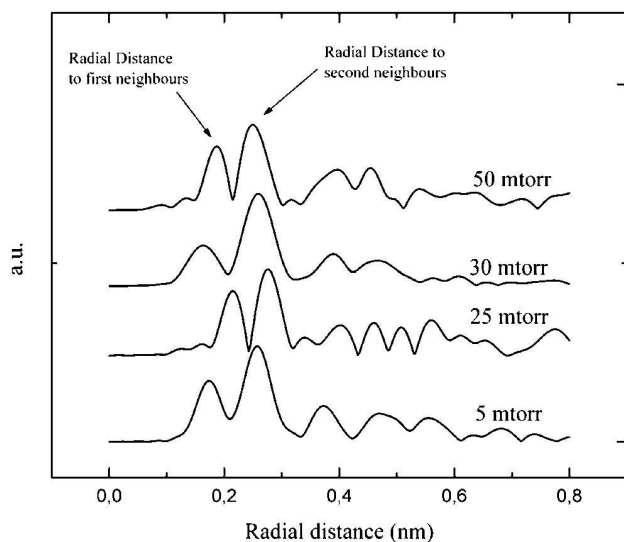


FIGURE 3. Radial distribution function obtained by applying the FFT to the spectra of Fig. 1.

is in 0.299 nm, corresponding to the first and second nearest neighbours. These numerical values must be corrected by the phase shifts process, which can be obtained using the Eq. (3). A complete set of results appears in Table I.

The remainder of the data analysis involves least-squares fits to the back-Fourier transformed peaks in  $k$ -space. Phase and amplitude parameters from de standard compounds are used. The parameters calculated are  $N$ ,  $R$ ,  $\Delta\sigma^2$ , and  $E_0$ ;  $\Delta\sigma^2$  is determined by relative to the standard.

$\chi(k)$  is a function of  $k$  and not  $E$  and  $k$  depends on  $E_0$ , and  $E_0$  is not related to any simple feature of the spectrum such as the inflection point. Accordingly,  $E_0$  is treated as an adjustable parameter in the data analysis. This can compensate for differences in bonding between the unknown and the standard  $\text{TiO}_2$ . The fitting procedure is a highly iterative process. The following is a typical procedure. Initially, the data are fitted in  $k$ -space, and four parameters,  $N$ ,  $R$ ,  $\Delta\sigma^2$ , and  $E_0$ , are allowed to vary. When a good fit is found,  $R$  and  $E_0$  are kept constants, and  $N$  and  $\Delta\sigma^2$  are allowed to vary. After  $N$  and  $\Delta\sigma^2$  are optimized, they are fixed, and  $R$  and  $E_0$  are allowed to vary. Fits in  $k$ -space are done with various  $k$  weighting factors, typically  $k^2$  and  $k^3$ . Fits are also checked in  $R$ -space using both the real and imaginary parts of the Fourier transform. The later is an important check for the presence of overlapping coordination shells and the correctness of the assumptions about the nature of the coordinating atom.

The numerical values for the first and second nearest neighbors obtained in this work and their respective known crystallographic values are in good agreement. The coordination number was also calculated with an ab-initio approximation using the model compound by using the FEFF 8.0 software. In this case the differences among the coordination numbers for each shell were similar to those reported in the literature.

#### 4. Conclusions

XANES analysis provides a valence of the TiN thin films growth by the sputtering technique. These analyses show that the film grown at 25 mTorr corresponds to the  $\text{Ti}_1$ . On the other hand, the atomic positions for the first and second nearest neighbors of the  $\text{Ti}_x\text{N}_y$  samples were derived by using the EXAFS experiments. The distances obtained after applying phase shift corrections are in good agreement with the known crystallographic values. The coordination number and  $\sigma^2$  were determined by using the FEFF 8.0 software.

EXAFS is one of the most ancient techniques for analysis of the structural parameters of a wide number of materials. EXAFS assisted by an ab-initio fit can be extended to provide very good structural information using the extended fine structure.

#### Acknowledgments

The author would like to acknowledge to the Centro de Investigación en Materiales Avanzados, S. C. for the technical support.

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1. Y.G. Shen, Y.W. Mai, W.E. McBride, Q.C. Zhang and DR. McKenzie, *Thin Solid Films* **372** (2000) 257.
  2. Y.G. Shen and Y.W. Mai, *Appl. Surf. Sci.* **167** (2000) 59.
  3. D.B. Chrisey and G.K. Hubler (Eds.), *Pulsed Laser Deposition of Thin Films* (Wiley, New York, 1994).
  4. H.D. Gu, K.M. Leung, C.Y. Chung, and X.D. Han. *Surface and Coatings Technology* **110** (1998) 153.
  5. C.J. Powell, A. Jablonski, I.S. Tilinin, S. Tanuma, and D.R. Penn, *J. Electron Spectrosc. Relat. Phenom.* **9899** (1999) 1.
  6. J.H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* **8** (1976) 129.
  7. M. Repoux, E. Darque-Ceretti, M. Casamassima, and J.P. Contour, *Surf. Interface Anal.* **16** (1990) 209.
  8. J.H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* **8** (1976) 129.
  9. C. Kittel, *Introduction to solid state Physics*, 6th edition (John Wiley & Sons Inc. New York, 1986).
  10. S. Tougaard, *Surf. Interface Anal.* **11** (1988) 453.
  11. C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, and G.E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Praire, MN USA, 1979.
  12. I. Bertoti, M. Mohai, J.L. Sullivan, and S.O. Saied, *Appl. Surf. Sci.* **84** (1995) 357.
  13. F. Esaka *et al.*, *J. Vac. Sci. Technol. A* **15** (1997) 2521.
  14. M.F. Doutora and Montemor. Instituto Superior Técnico. IN-ESC, Lisbon. Juiho de 2002.
  15. P. Lin *et al.*, *J. Vac. Sci. Technol. A* **5** (1987) 2732.
  16. Fu-Hsing Luu and Hong-Ying Chen., *Surface and Coatings Technology* **130** (2000) 290.
  17. BryCoat Inc. Ah rights reserved. Copyright ©2003.
  18. K.A. Pischow *et al.*, *Surf. Coat. Technol.* **67** (1994) 85.
  19. M. De Crescenzi, *Solid State Comm.* **90** (1981)613.
  20. M. De Crescenzi, *Surf. Sci. Reports* **21** (1995).
  21. E.A. Stern, D.E Sayers, and F.W. Lytle, *Physical Review* **11** (1975) 4836.
  22. JCPDS—INTERNL. CENTRE FOR DIFFRACTION DATA LICENSE 38-1420.
  23. A.G. MacKale, G.5. Knapp, and S.K. Chan, *Phys. Rey. B* **33** (1986) 841.
  24. A.G. McKale, G.5. Knapp, B.W. Veal, A.P. Pauhikas, and S.K. Chan, *Phys. Rey. B* **15**.
  25. Chance *et al.*, *Biochemistry* **35** (1996) 9014.