

# CHARACTERIZATION OF TITANIUM SILICON NITRIDE FILMS DEPOSITED BY PVD

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## Abstract

In recent years, nitride coatings have found widespread applications for tool and other hard surfaces. In this work the (Ti,Si)N system was investigated and some of its properties characterised. For this, (Ti,Si)N films with thicknesses ranging from 1 to 3.3  $\mu\text{m}$  and different contents of Ti and Si were deposited onto silicon wafers and polished high-speed steel substrates by r.f. reactive magnetron sputtering technique. The atomic composition of the samples were measured by Rutherford Backscattering Spectrometry (RBS).  $\text{Ti}_{1-x}\text{Si}_x\text{N}$  samples with  $0 \leq x \leq 0.37$  were produced. Regarding the structural properties, two cubic crystallographic structures were found, with lattice parameters of about  $a = 4.29 \text{ \AA}$  and  $4.18 \text{ \AA}$ . The grain size evaluated by Fourier analysis of X-ray peaks ranges from 5 nm to 34 nm. Concerning the adhesion results, the  $\text{Ti}_{1.70}\text{Si}_{0.30}\text{N}$  and  $\text{Ti}_{1.87}\text{Si}_{0.13}\text{N}$  sample presented the best results in adhesion with a critical load for total failure around 115 N and 105 N, respectively.

## 1. Introduction

In recent years there has been increasing interest in the deposition of composite films to answer the scientific and technological requirements in searching for new coating materials. One of the most well known examples is the deposition of TiN based composites that have found widespread applications for tools and other hard surfaces [1-7]. In accordance with the foregoing analysis, it has been found that its properties, namely physical and mechanical, can be improved by the presence of

some less noble elements, where Al and Cr are two of the most well studied. In order to further improve TiN performance, other transition-metal and alloy nitrides grown by physical vapour deposition process such as MoN, HfN etc. have also been the subjects of extensive research, showing significantly improvements, specially, in their mechanical properties. In this work we present some results on the behaviour of TiN coating with Si addition. With this, it is our main objective to gain a better understanding of the changes in the physical and mechanical properties of (Ti,Si)N induced by the changes in the composition of the matrix, which induces itself important changes in the texture of the coating. So, we intend to accomplish this task by examining the role of Si content and crystal structure of the nitride in the behaviour of thin films.

## **2. Experimental Details**

Polished high speed steel (AISI M2) and silicon substrates were coated with (Ti,Si)N films by reactive r.f. magnetron sputtering from high purity Ti and Si targets. Depositions were carried out in an Ar/N<sub>2</sub> atmosphere in an Alcatel SCM650 system. All substrates were sputter etched for 15 min. in a pure Ar atmosphere with 200 W r.f. power. The target to substrate distance was kept at 60 mm in all runs and the substrate holder was rotating over the targets at a constant frequency of 8 rpm. The base pressure in the deposition chamber was about 10<sup>-4</sup> Pa and rose to about 4x10<sup>-1</sup> Pa during depositions. The substrates were heated to 300 °C and a d.c. bias ranging from +25 to -75 V was applied. The experiments were carried out with the titanium and silicon targets coupled to r.f. sources (13.56 MHz), with powers in the range of 1.9 - 3.2 E+4 W.m<sup>-2</sup> for Ti and 1.8 - 2.3E+4 W.m<sup>-2</sup> for Si. The scratch tests were performed in a computer controlled Sebastian five - A (Quad group) scratch tester fitted with an acoustic detector. The tests were conducted with fixed conditions: a 200 µm diamond tip, a constant scratching speed 1E-4 m/s and a loading rate of 1.2 N/s. Five tests were performed in each sample. The atomic composition of the as deposited samples was measured by RBS. Ball cratering tests were conducted in the samples in order to determine the thickness of the films. X-ray diffraction (XRD) experiments were performed in a Philips PW 1710

apparatus using a Cu  $K_{\alpha}$  radiation and used for texture and grain size determination. The deflection method was used to evaluate the residual stress.

The grain size was evaluated from Fourier analysis of X-ray diffraction line profiles. In our samples only one first order diffraction profile is usually available. Thus, it was used the method introduced by Mignot and Rondot [8], based in the analysis of a single X-ray profile. This method uses a hyperbolic law to describe the microstrain term,  $\overline{\epsilon}_n^2 = C/n$ , in which, n is the harmonic number of the Fourier coefficients. A two degree polynomial is fitted to the Fourier coefficients, which polynomial parameters give the grain size.

### 3. Results and Discussion

#### 3.1. Characterisation of the as deposited samples

The samples were divided in two groups. The first group includes the samples grown with the same deposition parameters, except with different bias voltage (between -75 V and +25V), maintaining approximately constant the composition ( $Ti_{0.87}Si_{0.13}N$ ). The second one includes the samples grown with a bias of -50 V, but with different applied powers to each target, in order to get a different Ti and Si content. Table 1 presents the thickness (ball cratering) and atomic composition (RBS) of the samples of group 2. Regarding the texture, figs. 1a and 1b show X-ray diffraction patterns of the as deposited  $Ti_{1-x}Si_xN$  films. Fig. 1a represents the XRD patterns as a function of the Si composition and fig. 1b shows the XRD patterns as a function of the bias voltage. Those patterns revealed the presence of two crystallographic structures, both indexed to the cubic structure, one with a lattice parameter of about 4.29 Å (phase 1) and the other with a lattice parameter of about 4.18 Å (phase 2).

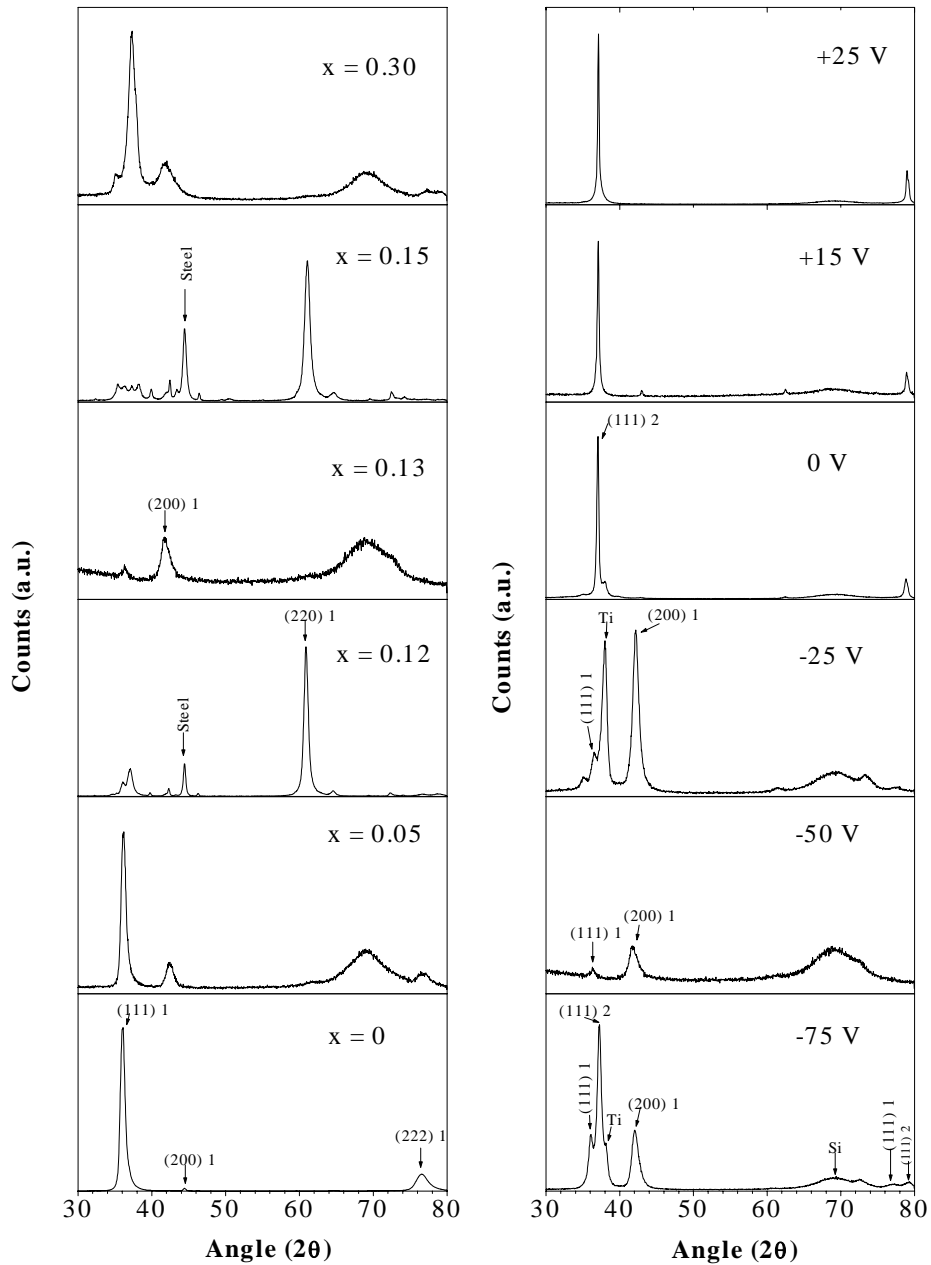
The changes in the bias voltage induced some changes in the relative fraction of each phase. Regarding the samples deposited with bias values of 0, 15 and 25 V, only the phase 2 with a (111) preferred orientation was observed, revealing relatively large grains (23, 25 and 34 nm,

• **Table 1.** - Thickness, composition and grain size of the samples.

Coating	Ti (at. %)	Si (at. %)	N (at. %)	Thickness ( $\mu\text{m}$ )	Grain size (nm)
TiN	50	-	$50 \pm 3$	3.3	7.4
Ti <sub>0.95</sub> Si <sub>0.05</sub> N	47.5	2.5	$50 \pm 3$	1.1	7.9
Ti <sub>0.88</sub> Si <sub>0.12</sub> N	44	6	$50 \pm 3$	3.3	9
Ti <sub>0.87</sub> Si <sub>0.13</sub> N	43.5	6.5	$50 \pm 3$	0.9	5
Ti <sub>0.85</sub> Si <sub>0.15</sub> N	42.5	7.5	$50 \pm 3$	2.1	6.2
Ti <sub>0.70</sub> Si <sub>0.30</sub> N	35	15	$50 \pm 3$	1.1	5 - 6
Ti <sub>0.63</sub> Si <sub>0.37</sub> N	31.5	18.5	$50 \pm 3$	1.7	4.8

respectively). On the other hand, phase 1 was observed for the samples deposited with a bias voltage of -25 V and -50 V, both with a (200) preferred orientation, and a grain size of 7.2 and 5 nm, respectively. For a bias voltage of -75 V, a mixture of the two phases was observed, the phase 2 with a (111) orientation and phase 1 with (111) and (200) orientation and a grain size of 5.5 nm.

As a function of the Si content, the sample with low Si content ( $x=0.05$ ) was found to grow on the (111) preferred orientation of phase 1. The samples Ti<sub>0.88</sub>Si<sub>0.12</sub>N and Ti<sub>0.85</sub>Si<sub>0.15</sub>N have a (220) preferred orientation. The samples with  $x = 0.13$  and  $x = 0.30$  have a (200) orientation. For all these samples only phase 1 was observed. The values of grain size, as a function of Si content, are shown in table 1.



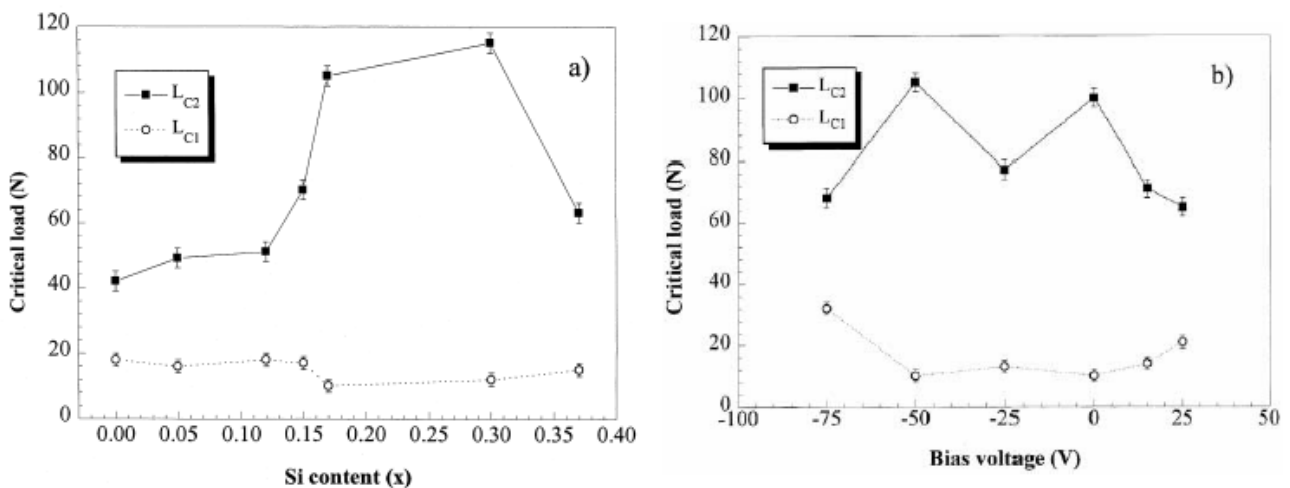
**Fig.1** - X-ray diffraction patterns of  $Ti_{1-x}Si_xN$  films with **a)**  $0 \leq x \leq 0.37$  and **b)** a bias voltage between -75 and 25 V..

### 3.2. Adhesion

When considering the performance and durability of a coating/substrate system, the adhesion of the coating to the substrate is certainly one of the most important properties to consider. The amount of energy required to separate a coating from the substrate is considered to be the adhesion strength. Anyway this energy is very difficult to measure, and so the required force to separate the coating from the substrate is often used as an indicator of the adhesion strength. From the several testing methods of evaluating the strength of adhesion, the scratch adhesion testing is in this matter,

one of the most commonly used technique. In this technique, and for the minimum load at which a failure occurs is called the first critical load  $L_{C1}$ . The load at which more than 50 % of the coating is removed from the substrate is called the second critical load  $L_{C2}$ . Once determined, these two critical loads are representative of coating adhesion. While in the detection of  $L_{C1}$ , optical observation is the most reliable method, the detection of  $L_{C2}$  can be achieved not only by optical observation, but also by the analysis of the acoustic emission and the frictional force curve, where total failure is obtained at the inflection point of the increasing frictional force curve [9].

The acoustic emission signals obtained during scratch testing were very difficult to interpret in this region of loading, although the first failures were nearly ever associated with a sudden increase in the acoustic signal. For the determination of the second critical load, the three methods were used together in order to minimise the error in the  $L_{C2}$  evaluation. Fig. 2 show the critical loads for (Ti,Si)N samples obtained by averaging the data for five different scratches in each sample. The standard deviation evaluated from experimental data varied between 1 and 2 N for  $L_{C1}$  and 2 and 3 N for  $L_{C2}$ .



**Fig.2** - Critical loads of  $Ti_{1-x}Si_xN$  samples as a function of the a) Si content and b) bias voltage.

The first note that becomes clear from the observation of fig. 2a is that the  $Ti_{1-x}Si_xN$  system reveals a significant increase in the load values for total failure when compared with that of TiN. For this system, higher  $L_{C2}$  critical loads were obtained for the  $Ti_{0.87}Si_{0.13}N$  (105 N) and  $Ti_{0.70}Si_{0.30}N$  (115 N), which show a very small grain size, in the order of 5 nm. Although the  $Ti_{0.63}Si_{0.37}N$  shows a

very small grain size, the critical load for total failure is relatively small, which we believe it might be due to the relatively high Si content. Anyway it is also clear that regarding the Si content, the results are not conclusive to infer about its influence in the adhesion behaviour. On the other hand, a closer look to the X-ray diffraction patterns on figure 1a shows that the two coatings that reveal best adhesion results show a (200) texture, while those with the lowest critical load values revealed a preferential growth on the (220) and (111) orientations. Not only the texture but also the grain size seems to be important for the improvement of the adhesion behaviour. The samples with  $x = 0.12$  and  $x = 0.15$ , which grew on the (220) direction, are a particular example of this. The one with the smallest grain size shows exactly the highest critical load value.

Regarding the bias voltage (fig. 2b), the samples produced at -50 and 0 V revealed the highest critical adhesion values. Concerning the grain size and texture, one can distinguish two different groups. The first one with very small grain sizes (between 5 and 7.2 nm) and a (200) preferred orientation, which were produced with negative bias. The second presents large grains ( $> 23$  nm) and a strong (111) orientation, and were produced with positive bias. In this group the best critical load values were obtained for the sample produced with a bias of 0 V, to which corresponds the smallest grain size. Similar behaviour was observed in the first group where the sample with the smallest grain size presents the higher critical load. From these observations one can infer that not only the grain size but also the texture, are determinant for the coating adhesion behaviour.

No significant changes were observed for the first critical load values.

### **3.2. Intrinsic stress**

It is well known and established that both mechanical and tribological properties of a coated sample are very much affected by the greatness and relative spatial distribution of residual stresses [10]. As an example of this, G. Kleer and co-workers have found that a high compressive stress field within the coating is the responsible for an increase in its fracture toughness. Anyway it is well known that excessive compressive stresses may provoke adhesion damages to the samples, mainly

around the edges. Generally, this stress level is in the range of  $10^{-2}$  and  $10^2$  GPa, which can be of a compressive nature when the film try to expand parallel to the substrate surface or buckle up from the substrate; or of a tensile nature when the films tends to contract parallel to the substrate which sometimes tend to the development of cracks. One of the most important components for the total stress observed in a coating is its intrinsic stress which is a result of several factors such as lattice mismatch between substrate and film, incorporation of impurities, rate of the deposition of the film, among others. This intrinsic stress can be measured by a series of techniques. In this work the deflection method was used, consisting of measuring the curvature induced in the substrate by the stress of the film and using the Stoney equation [11]:

$$\sigma = -\frac{E_s}{6(1-\nu_s)} \cdot \frac{t_s^2}{t_f} \cdot (r_a^{-1} - r_b^{-1}) \quad (1)$$

where  $E_s/(1-\nu_s)$  refers to the biaxial modulus of the substrate ( $E_s = 2070$  and  $\nu_s = 0.3$  [12]),  $t_s$  and  $t_f$  are the thicknesses of the substrate and film, respectively.  $r_b$  and  $r_a$  represent the curvature radii of the samples before and after deposition. To determine these curvatures, the samples (stainless steel discs with 25 mm diameter and 0.05 mm thick) were measured with a high resolution profilometer with a ruby tip. Following Ramsey, et al. work [13], a parabolic equation:

$$\delta(x) = a + bx + cx^2 \quad (2)$$

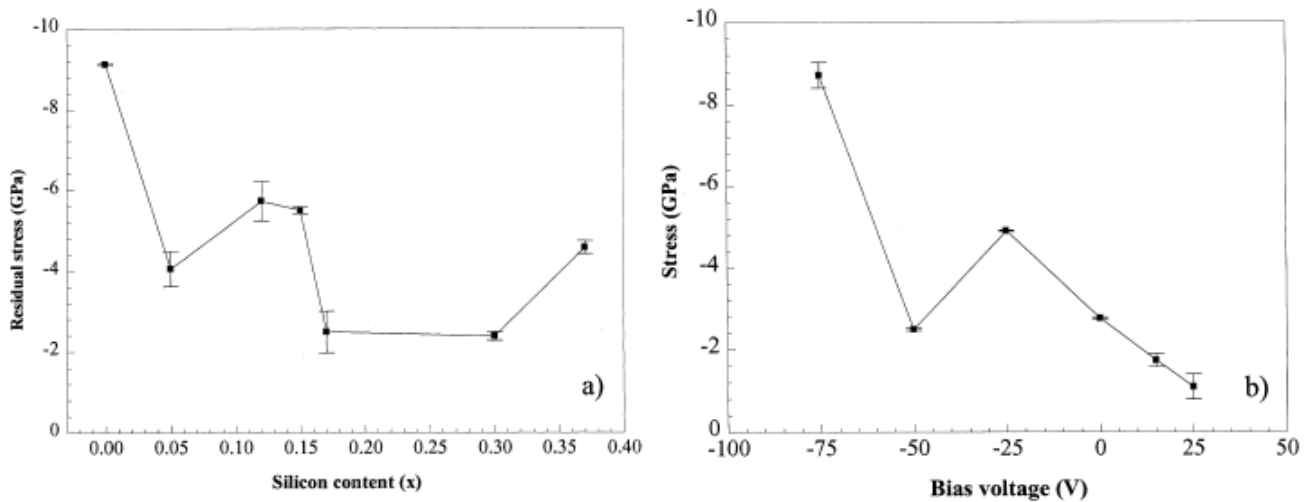
was fitted to the experimental data before and after deposition of the coating.  $\delta(x)$  represents the deflection of the sample as a function of the sample lateral length and a, b and c constants. The radius of curvature is then obtained from:

$$r = -\frac{1}{2c} \quad (3)$$

In respect to the residual stress results as a function of the Si content (fig. 3a), a significant decrease observed with the Si introduction when compared to the TiN sample. This decrease is even more pronounced for the  $Ti_{1.87}Si_{1.13}N$  and  $Ti_{1.70}Si_{1.30}N$ , which are the samples that revealed the higher critical adhesion loads. The residual stress results are somewhat correlated with the thickness of the samples, corresponding the highest residual stress values to the thicker samples. Regarding the



results as a function of the bias voltage (fig. 3b), the samples produced with the highest bias value (0, 15 and 25 V), and growing in the (111) preferred orientation, revealed the lowest values.



**Fig.3** - Evolution of intrinsic stress in respect to the **a)** Si content and **b)** bias voltage.

#### 4. Summary

The  $Ti_{1-x}Si_xN$  system revealed a significant improvement in adhesion behaviour when related to that of TiN. For this system, higher  $L_{C2}$  critical loads were obtained for the  $Ti_{.87}Si_{.13}N$  (105 N) and  $Ti_{.70}Si_{.30}N$  (115 N), which show a very small grain size, in the order of 5 nm. These two coatings show a (200) texture, while those with the lowest critical load values revealed a preferential growth on the (220) and (111) orientations. In these cases, is not only the grain size but also the texture seems to be important for the improvement of the adhesion behaviour.

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