Appl Phys A (2013) 110:957–961
DOI 10.1007/s00339-012-7227-5

**Applied Physics A**
**Materials Science & Processing**

# Tribological characterization of TiCN coatings deposited by two crossed laser ablation plasma beams

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Received: 23 May 2011 / Published online: 12 September 2012

**Abstract** The simultaneous laser ablation of two targets (graphite and titanium) in an Ar-$N_2$ gas mixture was carried out to deposit thin films of the ternary compound TiCN at room temperature. The base conditions used to produce the TiN without carbon were taken from our previous studies. The experimental conditions for the ablation of the carbon target were varied so that the carbon content in the films could be changed depending on the carbon ion energy. The control of the experimental conditions was carried out using a Langmuir planar probe which permitted the determination of the mean kinetic ion energy. The maximum hardness value of 35 GPa, was obtained with a carbon ion energy of about 250 eV, which corresponds to a film with 5 at% carbon content. In order to perform tribological and scratch tests, two types of substrate were used: nitrided AISI 316 stainless steel and AISI 316 stainless steel previously coated with a thin titanium layer (∼50 nm). Values of the wear rate in the range of $1.39 \times 10^{-6}$ to $7.45 \times 10^{-5}$ $\text{mm}^3\,\text{N}^{-1}\,\text{m}^{-1}$, friction coefficient from 0.21 to 0.28 and adhesion from scratch test measurements up to 80 N for final critical load, were obtained.

## 1 Introduction

The use of intense pulsed lasers for the deposition (PLD) of thin films has become a widely used technique, both in vacuum or in a reactive atmosphere. An important feature of PLD is the relatively high kinetic energies of the ablated particles, which enhances the atom surface mobility on the growing films thus allowing the deposition of crystalline materials even on substrates at room temperature. The simultaneous ablation of two targets, so that the expanding plasmas could interact, was proposed to reduce splashing or for the formation of alloys in vacuum [1, 2]. Based on these ideas, the use of simultaneous ablation of two targets in a reactive atmosphere was recently proposed in order to form thin films of ternary compounds. We call this arrangement Reactive Crossed Beam Pulsed Laser Deposition (RCBPLD), and it has been previously used to deposit TiCN thin films with different characteristics depending on the experimental conditions used for the deposition [3, 4]. Several publications have reported the use of Cross-Beam PLD to deposit YBCO [5], binary alloys of Fe-Al and Co-Cu [6], multilayers of Ni-C and Cross-Beams production of C, Ni, Sn, Fe-C alloys [7] but we have found no reports of the formation of ternary compounds using reactive Cross-Beam PLD.

The modification of TiN by adding carbon has been used as a way to enhance the properties of TiN [8]. In this work the RCBPLD configuration was used to deposit TiCN thin

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films, where the carbon content was varied as a function of the kinetic energy of the carbon ions, with this being determined using a Langmuir probe. The tribological performance and adherence of the coatings was measured as a function of the plasma ion energy.

## 2 Experimental

### 2.1 Experimental setup

The laser ablation system used in this work consisted of a vacuum chamber evacuated by a diffusion pump to a base pressure of $3.9 \times 10^{-4}$ Pa. During the deposition the chamber was backfilled with a 60/40 Ar/$N_2$ gas mixture to the working pressure of 1.07 Pa. The laser ablation was performed using a Nd:YAG laser with emission at the second harmonic (532 nm) and a 5 ns pulse duration. To obtain the thin films of the ternary compound, ablation was carried out simultaneously on two perpendicularly placed targets (Ti and C). The laser beam was divided into two beams; one of which was directed onto the titanium target and the other onto the carbon target. The energy fluence incident on the titanium target was kept constant at 25 J/cm$^2$ whilst the fluence on the carbon target was varied in the range between 5 and 55 J/cm$^2$ in order to study the effect of the different carbon plasma parameters on the characteristics of the deposited films. The substrate holder was placed in front of the titanium target at a distance which could be varied from 3 to 4 cm; previous experiments had shown that the ion energy and plasma density could be varied in a controlled manner by a combination of the substrate-target distance and the laser fluence on the target. The laser fluence is, in turn, a combination of the laser intensity and the spot size on the target. In this way, films could be prepared at different values of the carbon ion energy. Films were deposited at room temperature onto 2.0 cm diameter, 0.3 cm thick polished AISI 316 steel substrates. Given that the deposition of TiCN onto untreated substrate has a very poor adherence; two types of treatment were performed to the substrates before the deposition. For one of the series, labeled Ti-Layer Subs, a thin titanium coating of about 50 nm was deposited on the substrates and for the second series, labeled Nitrided Subs, a plasma nitriding treatment of the surface was performed to form a 1 µm nitrided layer with a surface hardness of approximately 9 GPa, using experimental conditions as described in article by E. Camps et al. [9].

The laser fluence on the titanium target was chosen from previous experiments of the deposition of TiN thin films and was kept constant [3]. These conditions were chosen to give TiN films that were crystalline (111), hard (24 GPa), and with average grain size of 15 nm the details of the experimental conditions and results concerning TiN can be found in Ref. [4]. The laser fluence for the ablation of the C target was varied in order to obtain the ternary compounds and to study the influence of carbon plasma on the properties of the deposits.

### 2.2 Plasma characterization

The mean kinetic energy of ions was measured using a 0.3 cm diameter, 0.1 cm thick, Stainless Steel planar Langmuir Probe which was placed at the substrate position. In all the experiments the probe was biased at −40 V, where the ion current is saturated. The temporal variation of the probe current was obtained by measuring the voltage drop across a 15 Ω series resistor using a Tektronix TDS 3052B Oscilloscope. From these measurements, the Time of Flight (TOF) curves could be obtained and from these curves the mean kinetic ion energy was calculated for each of the experimental conditions used for the deposition of the films. The mean kinetic ion energy was calculated following the work of Bulgakova et al. [10].

### 2.3 Thin film characterization

The carbon content in the films was measured by XPS (X-ray Photoelectron Spectroscopy) and N-RBS (Non-Rutherford Backscattering Spectroscopy [11]). Nanohardness measurements were performed using a CSM Nanohardness tester with a Berkovich indenter, for the hardness measurements it was considered that there was no influence from the substrate since the indenter loads were chosen such that the penetration depth was less than 10 % of the film thickness. The Scratch tests were carried out using a Tribotechnic Millennium 100 equipment with a 1.58 mm diameter 100Cr6 steel ball, a loading speed of 100 N/min and a sample speed of 10 mm/min. The tribology measurements were performed on a CETR UMT reciprocating movement tester with tips made of 10 mm diameter polycrystalline polished alumina balls, using loads of 2 and 5 N, a reciprocating frequency of 5 Hz for 10 minutes and a 10 mm fixed indenter displacement amplitude. The film thickness and the wear tracks were analyzed with a Veeco Dektak 150 Profilometer (2.5 µm radius stylus), with the wear rate being calculated from the volume lost during tribological testing.

## 3 Results

In general, the uniformity of the films was acceptable. The thickness of the coatings was 700 ± 50 nm with the highest variation at the edges of the substrate. The roughness (Ra) was measured in areas of 1 mm$^2$ after de deposition of the TiCN on the Nitrided substrates was 115 ± 20 nm and 80 ± 10 nm on the Ti-Layer substrates.

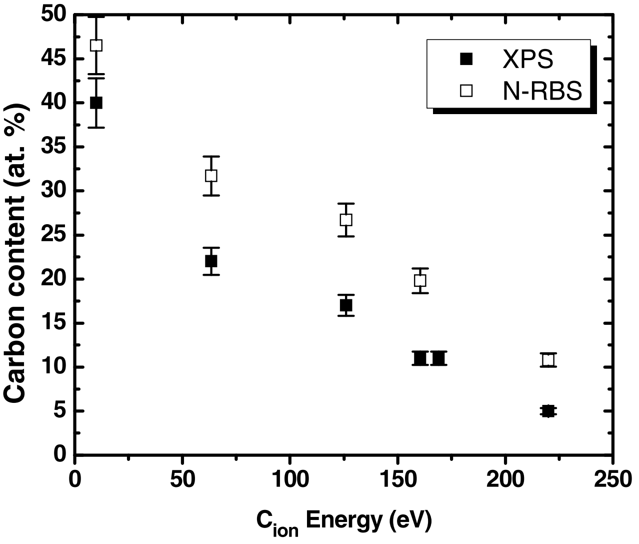

**Fig. 1** Carbon content of the TiCN thin films as a function of the carbon ion energy

## 3.1 Carbon content in the films

By changing the laser fluence on the carbon target, it was possible to vary the mean kinetic energy of the carbon ions incident on the substrate. Figure 1 shows the carbon content in the films as a function of the carbon ion energy with the same trend being observable for values from the two elemental analysis techniques used. The carbon content decreased as the ion energy increased; varying from 40 to 5 at.%. This result showed that TiCN films with different carbon contents could be deposited by controlling the carbon ion energy used during the deposition.

## 3.2 Hardness

The hardness of the films changed with the carbon ion energy. The highest value, of about 35 GPa, was obtained for a film deposited using an ion energy close to 250 eV, which corresponded to a carbon content of approximately 5 at. %. For values of ion energy greater or lower than this value the hardness decreased.

## 3.3 Coating adherence

As mentioned previously, two treatments to the substrates were performed in order to evaluate the mechanical properties of the coatings. Figure 2 shows the results for the final critical load, this being the applied force needed to completely remove the coating from the substrate. A trend can be observed towards decreasing values of the final critical load as the carbon ion energy increased. This indicated that the harder samples had a worst adherence; this may be associated to an accumulation of internal stress. For the case of nitrided samples the adherence improved when the carbon ion energy used for deposition was lower and the critical load was as high as 80 N. The use of medium values of carbon ion energy, between 90 and 180 eV, resulted in samples with hardness values around 30 GPa and final critical loads between 35 and 45 N. At present it is not clear why the critical load for the lowest ion energy was so different for the two types of substrate.

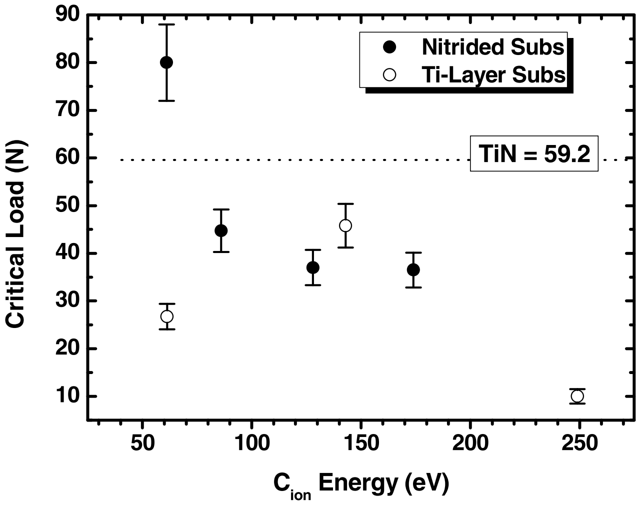

**Fig. 2** The critical load as a function of the carbon ion energy for the nitrided substrates and the Ti-Layer coated substrates; the dotted line shows the value of the TiN

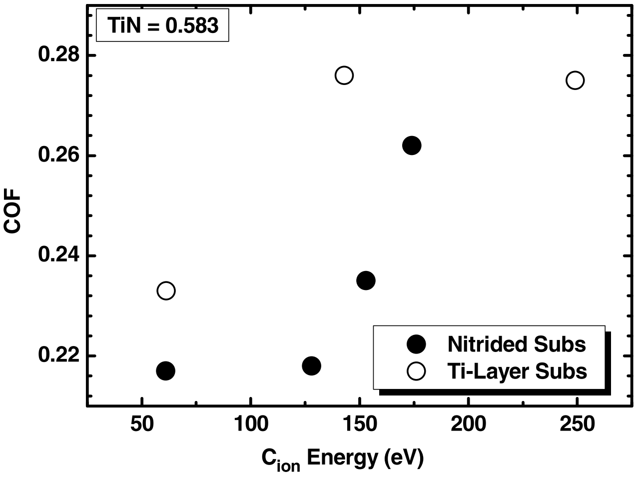

**Fig. 3** The coefficients of friction as a function of the carbon ion energy for both series of samples measured at 5 N loads. The values of the COF of the uncoated substrates were 0.637 and 0.438 for the nitrided and Ti coated substrates, respectively. The values of COF for the TiN are shown for comparison

## 3.4 Coefficient of friction

The Coefficient of Friction (COF) was measured during the wear experiments at two loads (2 and 5 N). The 5 N results

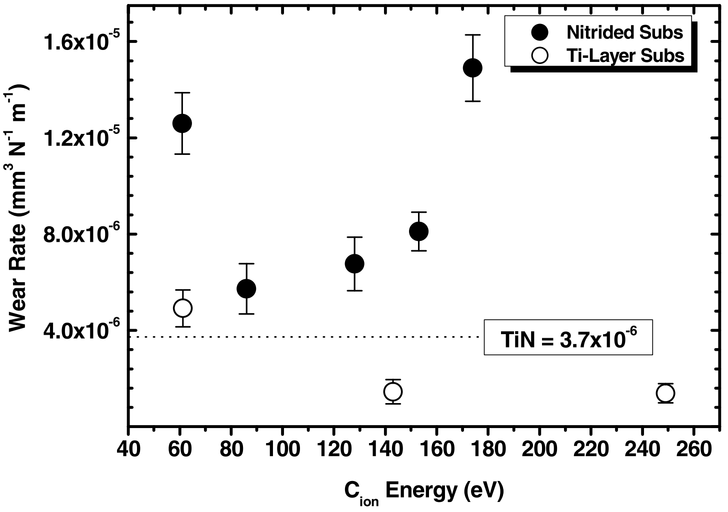

**Fig. 4** The wear rates of the films as a function of the carbon ion energy for the 2 N of applied load for the two series of substrates. The wear rate of the TiN film is shown for comparison

of these measurements are displayed in Fig. 3, it can be seen that all the values of COF for TiCN were less than that for TiN and both types of substrate. As mentioned earlier, films deposited at high carbon ion energies had lower concentrations of carbon and for these samples the COF tended to increase, as can be clearly seen in Fig. 3. No clear tendency of the COF with the ion energy was observed, but the results in all the cases were lower than those of the TiN. There was no significant influence of the substrate pretreatment on the COF results. The COF value for TiN is comparable to that reported elsewhere [12].

### 3.5 Wear rate

Figure 4 presents the results of the wear rates for the two types of substrate, measured at a load of 2 N. Most of the values are greater than that of TiN but less than that of the substrates without coatings which were $6.7 \times 10^{-5}$ and $4.3 \times 10^{-5}$ mm$^3$ N$^{-1}$ m$^{-1}$ for the nitrided and Ti coated substrates, respectively. In the case of the Ti layer pretreated samples, the wear rate showed a significant decrease as the carbon energy increased. The difference in the wear rate between the two types of substrate is possibly related to the implantation of carbon ions into the substrate underneath the Ti layer at the highest ion energies, with this forming some type of auto-lubricant carbon layer which reduces the wear rate. More work is required to clarify the observed results. The wear rates for the 5 N loads (not included in the figure) showed no clear variation as a function of substrate type or carbon ion energy and had an average value of $6.3 \times 10^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$. Even so, the obtained values, for all samples was in the range of $1.4 \times 10^{-6}$ to $7.5 \times 10^{-5}$ mm$^3$ N$^{-1}$ m$^{-1}$ which is comparable to those reported for coatings at least five times thicker [12].

## 4 Conclusions

In this work thin films of the ternary compound TiCN were deposited using the simultaneous laser ablation of two targets in a reactive atmosphere (RCBPLD). With this arrangement it was possible to vary the carbon content in the films in a controlled manner via the control of the plasma parameters, mainly by controlling the ion energy of the carbon plasma. The variation of the ion energy, and therefore the carbon content, allowed for the production of TiCN thin films with different mechanical properties. Improved adhesion and lower friction coefficients could be obtained by using previously nitrided substrates. Nevertheless the best wear rates were obtained for substrates which had been previously coated with a thin Ti layer, even though these samples had inferior film adhesion.

**Acknowledgements** This work was partially supported by CONACYT under contract No. 128732.

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