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TiCN thin films grown by reactive crossed beam pulsed laser deposition

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Abstract In this work, we used a crossed plasma configuration where the ablation of two different targets in a reactive atmosphere was performed to prepare nanocrystalline thin films of ternary compounds. In order to assess this alternative deposition configuration, titanium carbonitride (TiCN) thin films were deposited. Two crossed plasmas were produced by simultaneously ablating titanium and graphite targets in an Ar/N_2 atmosphere. Films were deposited at room temperature onto Si (100) and AISI 4140 steel substrates whilst keeping the ablation conditions of the Ti target constant. By varying the laser fluence on the carbon target it was possible to study the effect of the carbon plasma on the characteristics of the deposited TiCN films. The structure and composition of the films were analyzed by X-ray Diffraction, Raman Spectroscopy and non-Rutherford Backscattering Spectroscopy. The hardness and elastic modulus of the films was also measured by nanoindentation. In general, the experimental results showed that the TiCN thin films were highly oriented in the (111) crystallographic direction with crystallite sizes as small as 6.0 nm. It was found that the hardness increased as the laser fluence was increased, reaching a maximum value of about 33 GPa and an elastic modulus of 244 GPa. With the proposed configuration, the carbon content could be easily varied from 42 to 5 at.% by changing the laser fluence on the carbon target.

1 Introduction

Pulsed laser ablation has been extensively used to produce a wide variety of materials as thin films. Particularly, two major advantages make this technique suitable for thin-film deposition of crystalline titanium nitride based materials. Firstly, the high energy of the species present in the plasma plume enhances surface mobility and thereby permits crystalline film growth even at room temperature; secondly, this technique offers the possibility of deposition in a reactive atmosphere even at high pressures [1]. Different variants of this technique have been proposed in order to improve some characteristics of the deposits, as well as to obtain new materials. An interesting alternative is the so-called Crossed-Beam Pulsed Laser Deposition (CBPLD) proposed by Gaponov [2]. CBPLD is based on the interaction of the laser ablation plasma with a gaseous pulse, in order to diminish splashing on the deposit. A further modification of CBPLD has been proposed by Gorbunov in order to grow thin films of metastable alloys, simultaneously ablating two different materials in vacuum [3–5].

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In this work, we have used a crossed plasma configuration where the ablation of two different targets in a reactive atmosphere is performed in order to prepare nanocrystalline thin films of ternary compounds. We call this arrangement Reactive Crossed Beam Pulsed Laser Deposition (RCBPLD). Titanium carbonitride (TiCN) thin films have been prepared in order to study this alternative configuration. Metal transition nitrides are of interest owing to their mechanical properties; particularly, the hardness, which is somewhat limited in binary compounds. It is well known that alloying is a very useful technique to increase hardness; however, the alloying element must be added in a controlled way in order to optimize the material's properties. In general terms, TiCN has been seen to show better characteristics than TiN: higher hardness, higher toughness and enhanced adherence [6]. Additionally, plasma characterization is a very important tool in order to understand the physical processes involved in the laser ablation process, as well as, during the thin film growth. It is worth mentioning that two perpendicularly propagating plasmas have been characterized by optical emission spectroscopy and Langmuir probe techniques [7, 8]. In this work, the plasma and thin film characterization of TiCN films prepared by Reactive Crossed Beam Pulsed Laser Deposition are presented.

2 Experimental

2.1 Experimental setup

The laser ablation system used in this work consisted of a vacuum chamber, evacuated by a diffusion pump, with a base pressure of 7×10^{-6} Torr, which was backfilled with a 40/60 Ar/N_2 mixture to the working pressure of 8×10^{-3} Torr. For the deposition of TiCN, two targets (Ti and C) positioned perpendicularly to each other, were simultaneously ablated in the Ar/N_2 atmosphere. The substrate holder was placed in front of the titanium target at a distance which could be varied from 3 to 4 cm. The laser ablation was performed using a Nd:YAG laser with emission at the second harmonic (532 nm) and a 5 ns pulse duration. Films were deposited at room temperature onto Si (100) and 2.0 cm diameter, 0.3 cm thickness AISI 4140 steel substrates. The experiments were performed keeping the same ablation conditions on the Ti target and varying the laser fluence on the carbon target. In this way, it was possible to study the effect of the carbon plasma, particularly, the effect of the carbon content on the characteristics of the deposited TiCN films.

2.2 Plasma characterization

Optical emission spectroscopy (OES) was used to detect the excited species present in the plasma. This was done using a Czerny-Turner-type spectrometer (Spectra Pro 500i), equipped with a fast-intensified charge coupled device (ICCD) (Princeton Instruments model 1024E). The measured spectral resolution of 0.2 nm is obtained with a 1200 g/mm at 435.8 nm and an entrance slit of 50 μm width. A 150 ns gate was used for photon detection. The light was collected by an UV–Vis fiber bundle placed at a side window of the ablation chamber approximately 25 cm from the plasma. Synchronization between the laser pulse and the ICCD was ensured using a fast detector.

Determination of the plasma parameters, i.e., the average kinetic energy of ions and the plasma density, was performed by the Time of Flight analysis (TOF) of the measurements carried out using a Langmuir planar probe (6 mm diameter). In all the experiments, the probe was biased at −40 V, where the ion current is saturated, monitoring the voltage through a 15 Ω resistor. The plasma density was determined from the maximum ion current across the resistor. Measurements were performed under the experimental conditions used for thin film deposition in an attempt to establish a correlation between plasma parameters and thin film properties.

2.3 Thin film characterization

Thin film composition was determined from NRBS (non-Rutherford Backscattering Spectroscopy) measurements performed in a Tandem Van de Graff Accelerator. The crystalline structure of the deposited films was determined by X-ray diffraction using a Siemens D-5000 diffractometer with a Cu–K_α radiation source ($\lambda_k = 1.5406$ Å); additionally, the microstructure was studied by micro-Raman spectroscopy (HR LabRam 800). The film thickness was determined with a profilometer (Veeco Dektak 150). Nanohardness measurements were performed using a CSM Nanohardness tester with a Berkovich indenter.

3 Results

3.1 Plasma diagnostic

The optical emission spectroscopy (OES) results of the titanium plasma in the N_2/Ar atmosphere revealed a very rich emitting plume due to the presence of Ti* (Ti I), Ti^+ (Ti II) and Ti^{++} (Ti III) excited species. It is worth noting that under the experimental conditions used in this work the most abundant specie was Ti^+ and no signal associated with N or TiN was detected by OES.

For the carbon plasma, the OES results showed that the excited species present in the plasma were fundamentally: CII (283.6, 290.6, 299.2, and 426.6 nm) and CIII (406.9 and 418.7 nm), these line intensities change as a function of laser fluence, as was reported earlier [9].

When the Ti and C plasma were combined, no signal from C was observed, in part because the Ti line intensities were two to four orders of magnitude higher than the C ones.

The Langmuir probe measurements were performed for the individual plasmas and also for the combined plasmas. The mean Ti ion kinetic energy was determined from the probe curves. The calculations were carried out assuming that the ions incident on the probe were predominantly Ti II, which was justified by the OES results discussed previously. Additionally, the Ti plasma density was calculated from the maximum values of current collected by the probe. The results showed that the titanium plasma parameters used for deposition were a mean Ti^+ kinetic energy (E_{Ti}) of 375 eV with a plasma density (D_{p}) of $1.5 \times 10^{14}\ \mathrm{cm}^{-3}$. These parameters can be combined as a product ($E_{\mathrm{ion}} * D_{\mathrm{p}}$), which describes the degree of bombardment incident on the film during deposition, in this case this was $5.4 \times 10^{16}\ \mathrm{eV\,cm}^{-3}$. As was mentioned in the experimental section, the laser fluence on the carbon target was varied in order to study the effect of the carbon plasma on the characteristics of the TiCN films. In this way, the mean C^+ kinetic energy was varied from 9.9 eV up to 300.0 eV, and the plasma density was changed from 4.9×10^{10} up to $2.3 \times 10^{13}\ \mathrm{cm}^{-3}$. Under these conditions, the degree of bombardment on the growing film due to the carbon plasma varied from 4.8×10^{11} to $6.2 \times 10^{15}\ \mathrm{eV\,cm}^{-3}$.

3.2 Thin film characterization

3.2.1 Composition

The composition of the deposited films was determined by NRBS and confirmed for some samples by XPS. The obtained results showed that the films contain carbon, titanium, nitrogen, and oxygen. It should be noted that oxygen was not deliberately introduced and its presence is attributed to the residual background gas, a more detailed study is underway in order to clarify this issue. In general terms, it was observed that the nitrogen and oxygen content did not depend on the deposition conditions, however, the carbon content strongly depend on the degree of bombardment as shown in Fig. 1. This result suggests that the carbon content in the film can be controlled through the C^+ bombardment, i.e., a higher carbon quantity is incorporated in the film when a lower degree of bombardment is used. This is a somewhat surprising result since a lower degree of bombardment implies less carbon in the plasma plume and, therefore, a lower carbon content in the film would be expected.

3.2.2 Hardness

The nanohardness of the thin films were measured under conditions that the substrate would not affect the results. The results showed that the deposited films had a hardness of between 17.5 and 32.8 GPa, depending on the plasma conditions used. Figure 2 shows the hardness values as a function of the degree of bombardment. It can be clearly observed that as the degree of bombardment by C^+ was increased, from 4.8×10^{11} to $2.2 \times 10^{15}\ \mathrm{eV\,cm}^{-3}$, the hardness increased from 17.5 GPa to a maximum value of 32.8 GPa. As the degree of bombardment continued to increase, the hardness decreased to 20.9 GPa. The hardness of the TiN films prepared without carbon was 24.0 GPa.

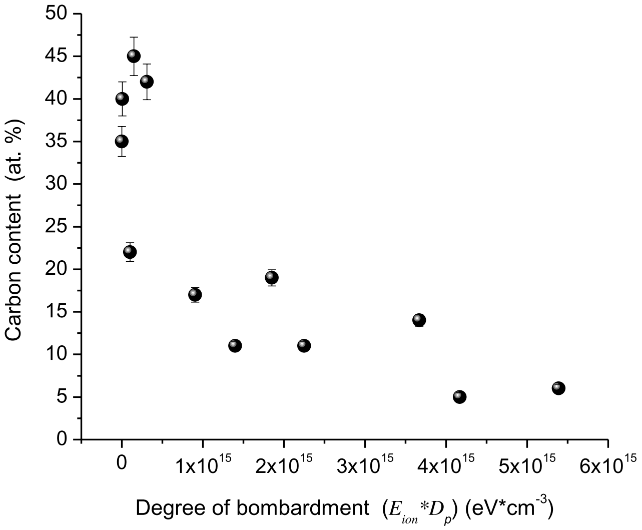


Fig. 1 The carbon content of the films as a function of the degree of bombardment

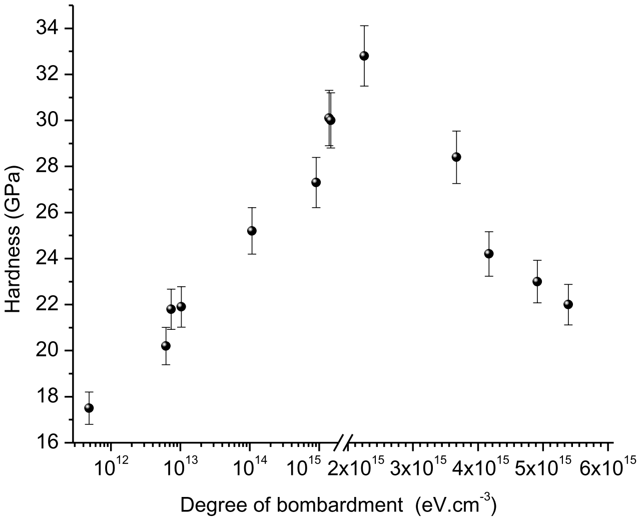


Fig. 2 The film hardness as a function of the degree of bombardment

It can be seen that the film hardness diminished as the carbon content was increased (see Fig. 3) and in fact there are two clearly defined regions. For carbon contents lower than 20 at.%, the hardness was greater than that of the TiN films, whereas for carbon contents greater than 20 at.%, the hardness values were lower than that of TiN films without carbon. The maximum hardness was obtained for an optimum carbon content of approximately 11 at.%. These results indicate that the carbon content has an important effect on the hardness film.

3.2.3 Structure

Structural characterization was performed by XRD and Raman spectroscopy, in part because Raman can provide information about the carbon bonding configuration. The X-ray diffraction patterns (not shown) were characterized by the presence of a peak at $2\theta = 35.99°$, which corresponds unambiguously to the (111) plane of cubic TiCN [10]. The fact that only the 35.99° peak was present indicates that the film preferentially grew in the (111) direction. This is an important result since the relationship between the (111) orientation and the resolved shear stress of the slip systems of TiN results in a harder material [11]. The average crystallite size as a function of the plasma parameters was estimated using the Scherrer equation. The results showed that the crystallite size was almost constant, approximately 6.5 nm, for the range of degree of bombardment by C^+ from 4.8×10^{11} to 1.1×10^{14} eV cm^{-3}. If higher degrees of bombardment were used, the grain size first increased to values of 16.0 nm at 2.2×10^{15} eV cm^{-3} and then diminished to 10.3 nm at 6.2×10^{15} eV cm^{-3}.

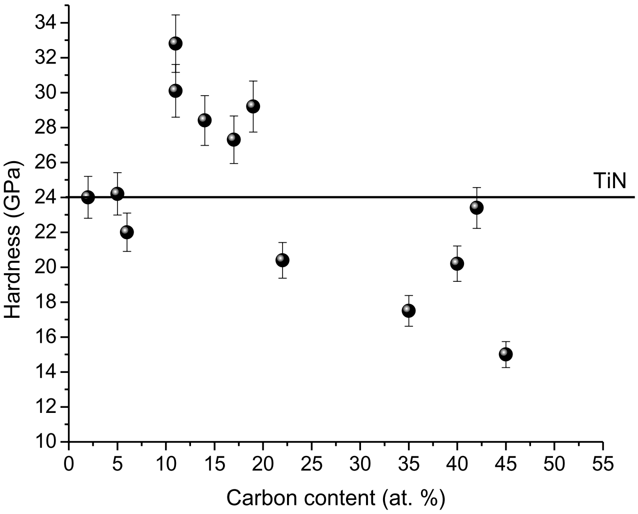
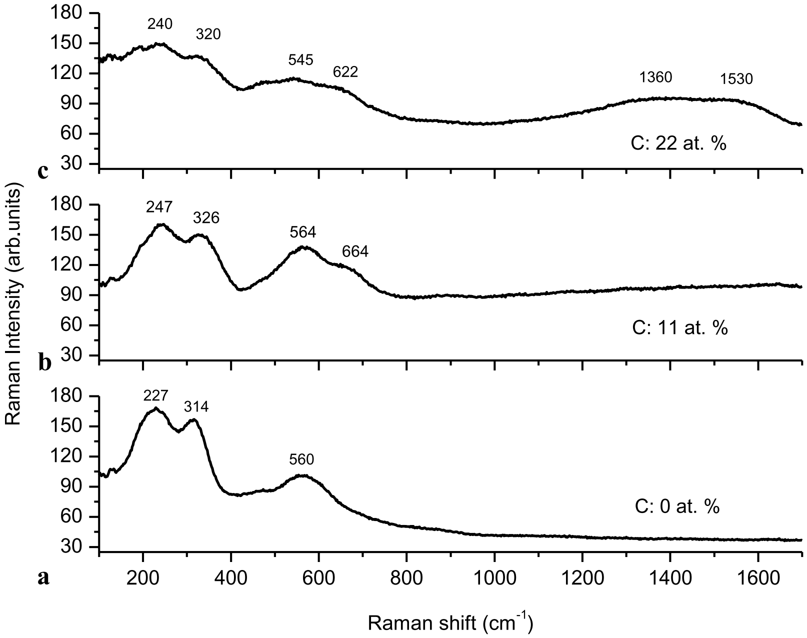


Fig. 3 The film hardness as a function of the carbon content

Figure 4 shows the Raman spectra corresponding to samples grown at different degrees of bombardment by C^+ and, therefore, different carbon contents. The lower spectrum (4a) is for a pure TiN film and is characterized by peaks at 227, 314, and 560 cm^{-1}; it should be noted that there are no features observed at higher wave-numbers. As the carbon content was increased, the Raman peaks shifted to higher wave-numbers: 247, 326, 564, and 664 cm^{-1} (spectra b and c), and this can be attributed to the formation of the TiCN ternary compound [12]. The results suggest that the carbon atoms are occupying nitrogen sites in order to form TiCN. Some samples were measured by XPS, and the presence of Ti–C bonds was observed, confirming the TiCN formation. Additionally, spectrum c shows the appearance of Raman signals in the 1000–1600 cm^{-1} region with this being indicative of the presence of amorphous carbon [13]. This result suggests that if a lower degree of bombardment is used, the resulting film is a mixture of crystalline TiCN and amorphous carbon.

Fig. 4 Raman spectra for samples with different carbon contents



4 Conclusions

The results obtained in this work showed that it is possible to prepare ternary compounds using the Reactive Crossed Beam Pulsed Laser Deposition. TiCN thin films with maximum hardness of approximately 33 GPa were obtained by RCBPLD. An advantage of the proposed deposition configuration is the possibility of controlling the carbon content in an easy way. This is one of the key issues to be able to prepare materials with specific properties for tailored applications. Plasma diagnostics was used to control the deposition conditions and provided useful information to better understanding the physical processes involved in thin film deposition by laser ablation.

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