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# Thermal evaluation of TiN/$CN_x$ multilayer films

Mônica de Mesquita Lacerda[a,*], Júlio Miranda Pureza[b], José Fernando Fragalli[a], Ney Mattoso Filho[c], Yip-Wah Chung[d]

[a] Department of Physics, CCT – State University of Santa Catarina, Campus Universitário s/n, Joinville, SC 89223-100, Brazil
[b] Department of Mechanical Engineering, CCT – State University of Santa Catarina, Joinville, SC 89223-100, Brazil
[c] Department of Physics, Federal University of Paraná, Curitiba, Pr 81531-990, Brazil
[d] Department of Materials Science and Engineering at Northwestern University, Evanston, IL 60208, United States

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ABSTRACT

This work examines the thermal behavior and failure mechanisms of TiN/$CN_x$ multilayer coatings deposited by DC magnetron sputtering. The samples were examined by transmission electron microscopy before thermal analysis. During thermal analysis, the samples were heated up to 1070 K at a constant rate of 10 K $min^{-1}$ in a $N_2$ atmosphere and their thermal stability was evaluated by thermo gravimetric (TGA) and differential thermal analyses (DTA). These analyses indicate that the multilayer coating is thermally stable up to 950 K, followed by stress relaxation when the temperature exceeds 950 K. After this thermal treatment, coating surfaces were observed by scanning electron microscopy. Buckling and fractured surface were seen for multilayers deposited with and without substrate bias voltage applied during growth process, although samples deposited with substrate bias are more resistant to crack formation and propagation.



## 1. Introduction

Titanium nitride (TiN) and amorphous carbon nitride (a-$CN_x$) are both intellectually and technologically important materials. Titanium nitride (TiN) films have been studied [1] and applied in several industrial segments for over 20 years [2–5]. Normal deposition process often leads to a columnar structure, which is responsible for its failure under certain loading conditions [1]. Crystalline beta-carbon nitride ($\beta$-$C_3N_4$), a hypothetical material with the same structure as silicon nitride ($\beta$-$Si_3N_4$), was first predicted to be as hard as diamond [6], resulting in many research studies attempting its synthesis [7–14]. The growth of an oriented TiN (1 1 1) film that is structurally commensurate with the hypothetical $\beta$-$C_3N_4$ has been used to seed its growth, but such a crystalline $\beta$-$C_3N_4$ layer is only stable for no more than a few layers, beyond which amorphous $CN_x$ is grown [12]. It was noted that such an amorphous $CN_x$ layer can interrupt the growth of TiN columnar structure [13]. Further studies have shown that there is an optimum thickness ratio between TiN and $CN_x$ layers that result in high hardness and low internal stress [13].

As indicated by high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) and nanoindentation measurements, it is possible to investigate the relationship between microstructure and properties of TiN/$CN_x$ multilayers as a function of their nanolayer period and of the bias voltage applied to the substrate during sputter-deposition [13]. Generally, these multilayer films are harder and smoother than TiN single-layer films. Typically, a-$CN_x$ films deposited by reactive sputtering are soft and polymer-like with hardness ranging between 8 and 12 GPa [14] and TiN films deposited by DC magnetron sputtering achieve hardness up to 20 GPa. Nonetheless, TiN/$CN_x$ multilayers can reach hardness up to 40 GPa and the differences cannot be explained by the simple rule of mixtures [15,16]. This result makes TiN/$CN_x$ films potential candidates as protective coating against wear for many industrial tooling and products, which require surfaces with superior mechanical and tribological properties.

In order to evaluate TiN/$CN_x$ films applicability, it is necessary to analyze their thermal behavior and failure mechanisms. This paper evaluates the structure of TiN/$CN_x$ films deposited on silicon wafers before thermal analysis by transmission electron microscopy (TEM). Their thermal behavior was examined by differential and gravimetric thermal analyses (DTA and TGA) and scanning electron microscopy (SEM). TEM results show stressed coatings, and thermal analyses show thermal stability with no microstructure changes at temperatures as high as 950 K. SEM images show film

* Corresponding author. Permanent address: Pólo de Xerém/UFRJ, Estrada de Xerém, 27 Duque de Caxias, RJ 25245-390, Brazil. Tel.: +55 21 2679 6441; fax: +55 21 2679 2098.
*E-mail address:* monica_lacerda@joinville.udesc.br (M. de Mesquita Lacerda).

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buckling and cracks as a consequence of film–substrate interface stress release.

## 2. Experimental

$TiN/CN_x$ samples deposited on silicon (1 0 0) were synthesized using a dual cathode DC reactive magnetron sputtering system. The system base pressure was typically $1.0 \times 10^{-5}$ Pa, and the deposition pressure was kept the same for all experiments at 2.0 Pa. Pure titanium (99.9%) and pure graphite (99.99%) targets were sputtered in argon (Ar) and nitrogen ($N_2$) gas mixture. Titanium and carbon targets were both energized during deposition, and the current applied on each one was 500 mA and 150 mA, respectively. A computer-controlled shutter regulated the thickness of individual TiN and a-$CN_x$ nanolayers. $CN_x$ thickness ($h_{CN}$) is 0.75 nm for all samples studied, while TiN thickness ($h_{TiN}$) varies from 2.25 nm to 7.5 nm, i.e., TiN thickness is 3–10 times the thickness of $CN_x$, and the multilayer period ($\Lambda$) ranges from 3 nm to 8.25 nm, which is an important structural parameter determining final properties [17,18].

$TiN/CN_x$ films analyzed at this paper were deposited at 0 V and −200 V bias voltage ($V_b$), although samples grown at $V_b = -100$ V and at $V_b = -300$ V were also deposited. However, films deposited at −100 V reach hardness values nearby that obtained to TiN single layers or to $TiN/CN_x$ deposited at no bias voltage (0 V) with lower deposition rate. Furthermore, $TiN/CN_x$ films at −300 V are very hard, reaching hardness close to 40 GPa, nonetheless films present very low deposition rate and adhesion problems due to elevated internal stresses [13]. These results lead us to choose $V_b = 0$ V and $V_b = -200$ V, due to a set of characteristics obtained at this condition, such as high hardness, low roughness, not too stressed samples and acceptable deposition rate. Before $TiN/CN_x$ multilayer deposition, a 100 nm thick TiN buffer layer at no bias voltage was deposited to improve film adhesion to the substrate. The internal stress of this layer is low and typically 100 MPa. The total coating thickness ranges between 0.45 μm and 0.8 μm.

$TiN/CN_x$ multilayer surfaces were analyzed before thermal treatment by transmission electron microscopy (TEM) using a JEOL JEM 1200EX-II at 120 keV. Standard sample was used for calibration purposes of the microscope. $TiN/CN_x$ samples were cut ultrasonically and thinned in an acid solution of HF: $HNO_3$.

In order to evaluate thermal stability of the coatings, samples were investigated by simultaneous thermo gravimetric and differential thermal analyses (TGA and DTA) in a NETZSCH STA 449C – Geratebau GmbH – Thermal Analysis Proteus. A highly sensitive microbalance used in the TGA provides an accurate estimate of mass change during thermal analysis. Samples were heated at constant temperature rate of 10 K min$^{-1}$, up to 1070 K in $N_2$ atmosphere. An $Al_2O_3$ crucible was used as reference material due to its inertness. The silicon substrate is stable up to 1600 K and does not contribute to the DTA analysis. Surface topography and composition were analyzed before and after thermal analysis by scanning electron microscopy (SEM) and by energy-dispersive x-ray spectroscopy (EDS) at 20 kV by a Zeiss DSM 940A equipment.

## 3. Results and discussion

### 3.1. As-deposited samples

TiN and $TiN/CN_x$ films were investigated by transmission electron microscopy (TEM) in order to evaluate their crystalline structure before thermal treatment. Fig. 1a and b shows plan-view images and electron diffraction pattern taken from these samples. TiN films present a coarse grain structure, while $TiN/CN_x$ multilayer coatings are more homogeneous. Diffraction images reveal that both types of coatings are polycrystalline.

Expected interplanar spacing values ($d$) of TiN and measured values for TiN and $TiN/CN_x$ films are summarized in Table 1. The measured values are the same as, or slightly larger than the expected values by about 1–3%. This is due to stress inflicted to the samples (substrate + multilayer) during the deposition, either by crystal lattice parameter mismatch between film and substrate or by the energy transferred to the growing samples by the deposited ion. Cross sectional high resolution TEM images do not show the periodicity of the samples, although its diffraction pattern shows fully crystalline structures. The layer structure cannot be seen, since the thickness of individual $CN_x$ layers ~0.75 nm is comparable to the ion-mixing distance at 200 eV and 300 eV ion bombardment energy [13].

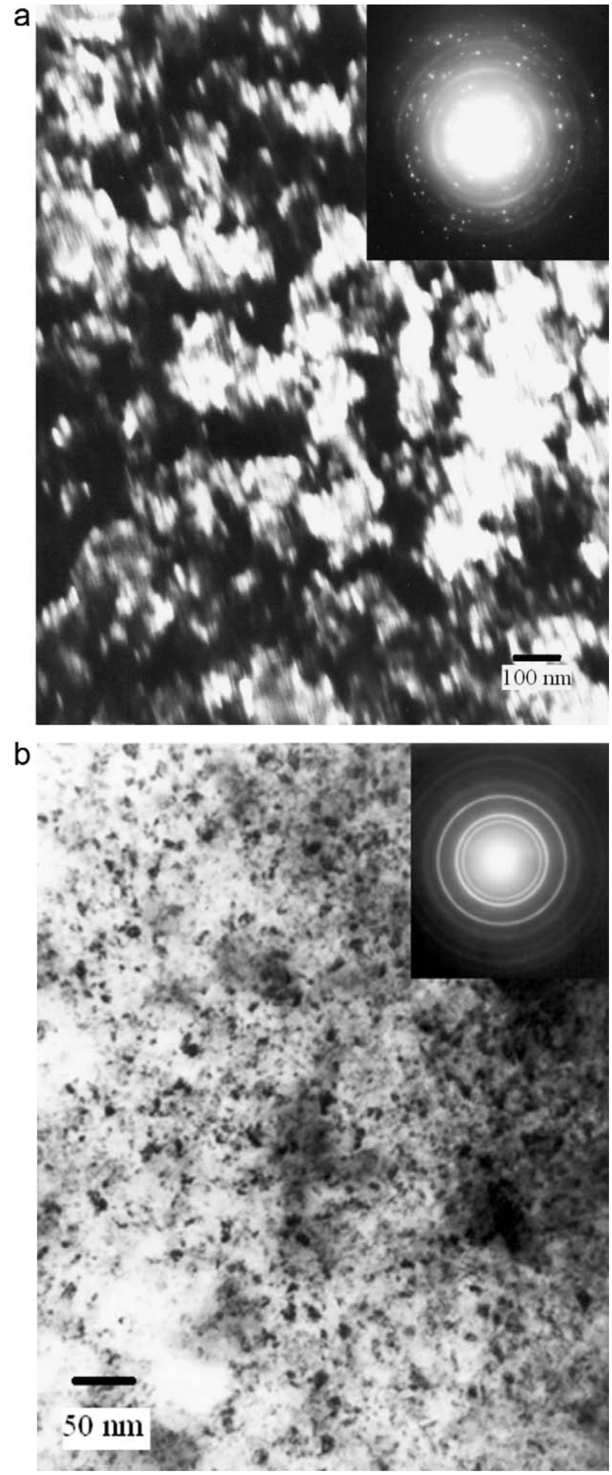


**Fig. 1.** TEM images and electron diffraction patterns before thermal annealing from: (a) pure TiN coating, (b) $TiN/CN_x$ multilayer coating. Samples were grown at $V_{bias} = -200$ V.

### 3.2. Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used to investigate the thermal evolution of the $TiN/CN_x$ films. This investigation is important in order to establish the use of these coatings at high temperatures, such as protective coating of steel tooling or steel molding for polymer and aluminum injection. All the evaluated samples had to be cut in very small