Synthesis and characterization of Nanostructured thin films by reactive triode sputtering

Chahinez Saied and Abdelouahad Chala

Laboratoire de Chimie Appliquée, Université de Biskra, BP 145 RP, 07000 Biskra, Algeria

Abstract

The present work deals with structural, mechanical and tribological charaterization of nanostructure of nitrides based films (ZrN, TiN) for cutting tool applications. Coatings are deposited by reactive magnetron sputtering from metallic targets (Ti, Zr and B) on static substrate holders with RF or DC bias.

Thermo chemical treatments by plasma nitrided have been held on steel substrates for eventual duplex applications.

The influence of plasma parameters (nitrogen partial pressure and substrate bias) on mechanical properties of ZrN an TiN is studied. In order to improve its mechanical properties, bore is then introduced to TiN and ZrN thin films. The fraction of bore into the coatings is then increased in order to achieve the formation of ZrBN and TiBN nanocomposite. Chemical, mechanical, tribological and structural properties are studied as a function of bore content using XPS, FTIR and nano-indentation, Scratch tests, XRD, SEM and TEM techniques. C-BN and h-BN phases are detected from 1 at.% of bore by XPS measurements.

An increase of the hardness is observed while adding bore to nitrides with two maximum at 5 and 10 at.% of bore. The resistance corrosion is also studied as function of deposition conditions.

Keywords: reactive magnetron sputtering, thin films, mechanical properties, tribological properties, TiN, ZrN, TiBN, ZrBN, nancomposites, corrosion.

Introduction

Cubic BN presents a variety of mechanical, thermal, electrical and optical properties [1] highly desirable for thin-film applications. The main problem for its industrial application is that c-BN films peel off from substrate even for low thickness (0.1 - 0.2μm). This delamination of c-BN films is attributed to high compressive stress, which is believed to arise from the intense energetic ion bombardment [2,3]. Many attempts have been made to improve the adhesion of c-BN films such as the introduction of intermediate buffer layers and the increase of the substrate roughness [4]. It was shown [5] that boron, boron-rich and boron carbide/B-C-N gradient layers increase c-BN film adhesion.

Nevertheless, these interfaces may be detrimental to some potential applications of c-BN films. Another way was to increase the deposition temperature. Taylor *et al.*[6] obtained thick adherent c-BN films at temperatures up to 1000 °C. But such a high temperature limits the number of possible substrate materials for c-BN growth. A third way was to decrease the stress level by post- deposition annealing or ions implantation. Kim *et al.* reported a stress decrease down to 3 GPa after 40 min annealing in nitrogen at 800°C [7]. Widmayer *et al.* [8] also observed a reduction of stress level, a graphitization and a resputtering of the films during ion implantation at high energy (50-100 keV).

Recently, some studies have shown that growing conditions are different from nucleation ones [9] and stress models of thin films deposited under ion bombardment predicts stress variation with ion energy and flux. [10, 11] What is generally called c-BN film is, in fact, a multilayer structure, which consists of an amorphous BN layer at the film/substrate interface, followed by a textured h-BN layer and the thick c-BN layer. Finally, at the top a very thin h-BN layer is observed [3]. In a previous paper [12], we have shown that a peak of stress of about 15 GPa is

observed in the h-BN basal layer, and that the occurrence of the cubic phase leads to a stress relaxation as expected from the conversion of the h-BN into a denser structure [12]. We may conceive to decrease the stress level, and thereby improving the adhesion, if we maintain a low value of stress by reducing the ion bombardment after the nucleation of the cubic phase. Bi-step procedure, where we have differentiated between the nucleation and growth conditions, has been used in order to decrease the stress level and improve the film adhesion. The results show a significant improvement of film adhesion. In fact for the films deposited by changing the ion fluxes, there were no delamination and no cracks in the film even after a long period. Scratch tests have been conducted and critical loads up to 5 N have been measured. Despite the adhesion improvement no stress relaxation was observed and the stress level remains as high as 10 GPa [13].

The purpose of the present work is to decrease the stress in the films by depositing a ternary compound like ZrBN. The addition of a third element like zirconium can be a means for achieving this goal and therefore improving in a significant manner the adhesion of the coating without an important decrease of its hardness thanks to the intrinsic hardness of ZrN.

Experimental Part

Triode Sputtering System (TS) was the deposition methods used in this study. It consists of a chamber pumped down to 5×10^{-5} Pa by a diffusion pump. An emitting filament and a plate anode create the plasma discharge. Two magnetic coils assure a high rate of ionization that enables to work at pressures down to 0.05 Pa. The target was dc biased, while the substrate holder was biased by a rf generator. A ZrB_2, nitrogen and argon gases were used [14]. For both the deposition techniques, silicon <100> substrates were used. The structural investigations of the deposited films were performed by IR absorption spectroscopy using a FTIR spectrophotometer (Biorad FTS 6000). The transmission spectra were recorded at normal incidence in the range of 400 to 4000 cm^{-1}. The hexagonal phase (h-BN) of boron nitride is characterized by the two infrared active TO modes which give a strong and asymmetrical absorption band E1u at approximately 1380 cm^{-1}, attributed to B-N-B bond in plane stretching, and a weaker band A2u near 800 cm^{-1} due to an out-of-plane B-N-B bond bending mode [3]. The zinc blend phase (c-BN) exhibits a single absorption band near 1065 cm^{-1} attributed to the infrared active TO mode. X-ray diffraction analyses using glancing angle with Co Ka radiations were performed to determine the structure of films.The mechanical stress was calculated from substrate curvature measurements.

The substrate Curvature and film thickness were measured by Dektak 3030 profilometer and gravimetry measurements were carried out using Sartorius Supermicro S4 microbalance. SEM and TEM observations were performed to determine the morphology and the microstructure of the coatings.

Results and discussion

The morphology of selected coatings deposited on low alloy steel is shown in the SEM photograph in Fig. 1.a. The Zr-B-N coatings exhibit a very dense structure. No columns nether grains were observed. Fig. 1.b. shows the microstructure of the films obtained by TEM. It reveals some ZrN crystallites in amorphous matrix.

Fig. 2 presents the X-ray diffraction patterns with 2θ scanning from 20 to 70 degrees as function of nitrogen flow and substrate bias voltage. It is clear that the preferred orientation is always (220). With increasing nitrogen flow (Fig. 2. b.) crystalline films growth slightly favoured with respect to amorphous growth. The transition from an amorphous to crystalline structure occurs in the nitrogen flow range from 12 to 19 sccm. Fig.2. a. shows the influence of the substrate bias voltage in the XRD patterns at a constant flow rate (12 sccm). The film structure changes from amorphous to crystalline with increasing substrate bias voltage. The

increasing of bias voltage and thus the higher ion energy during film growth enhances the activity of condensing particles resulting in an increased activity for the formation of the Zr B-N phase. Substrate bias voltage and nitrogen flow are the main parameters to obtain c-BN nucleation by triode sputtering system. Substrate bias voltage was firstly scanned from 0 to 150 V. fig. 3. a. shows the evolution of IR spectra for ZrBN films growths in pure nitrogen vs. bias voltage. T2 (1095-1100 cm^{-1}) peak of c-BN and E_{1u} (1395-1400) peak of h-BN were observed. Increasing substrate bias voltage is accompanied with decreasing of the intensity of h-BN peak and increasing of c-BN one. The maximum amount of c-BN found (79 %) was obtained in the range of 75-100 V bias voltage. Fig.3. b. shows the FTIR spectra of Zr-B-N films prepared with different flow of nitrogen. It can be clearly seen that with increasing nitrogen flow rate the transmission peak corresponding to c-BN phase becomes stronger. This implies that B-N bonding were formed in zirconium boron nitride films. The maximum of c BN formed in this case was about 98 % and it was obtained in the range of 25-50 %.

The evolution of the stress within the films was calculated by the Stoney equation from the inverse of the curvature radius and the corresponding thickness. The calculated stress values obtained from each film are reported in Fig. 4. The internal stress is max at -100V, which is the optimum bias for max c-BN content. The level of stress is decreased by almost an order of magnitude.

Conclusion

ZrBN films have been deposited on silicon and low alloy steel substrates by triode sputtering of ZrB_2 composite target. The conditions of deposition were successfully controlled and the properties of the layers are defined as function of the nitrogen flow and the negative bias voltage. Bi step procedure enables to increase the adhesion of the c-BN films but it appears no relaxation of the internal stress. Compressive stress in BN appears to be more related to the c BN content than to the deposition conditions. Thick (2 μm), dense films constituted of nanocristallites of ZrN has been observed.

Narrow window of experimental conditions lead to c-BN phase is observed and the maximum is obtained for 75 % N_2 and -100 V bias voltage.

References:
[1] L. Vel, G. Demazeau and J. Etourneau, Mater. Sci. Eng. 1991, B10, 149.
[2] D.J. Kester, K.S. Ailey, D.J. Lichtenwalner, R.F. Devis. J. Vac. Sci. Technol. 1994, A12, 3074.
[3] P.B. Mirkarimi, K.F. McCarty, D.L. Medlin. Mater. Sci. Eng. 1997, R21, 47.
[4] R. Freudenstein, S. Reinke, W. Kulisch, R. Fischer, J. Zweck, A. Bergmaier, G. Dollinger, Mater. Sci. For., 1998, 259, 287.
[5] M. Keunecke, K. Yamamoto and K. Bewilogua, 7th Int. Conf. on Plasma Surface Engineering, Garmisch-Partenkirchen, Sept. 2000.
[6] C.A. Taylor and R. Clarke, Mat. Res. Soc. Symp. Proc. 1996, 423, 265.
[7] I.-G. Kim, S.-H. Kim and K.-B. Kim, J. Vac. Sci. Technol. 1998, A 16 (4), 2295.
[8] P. Widmayer, P. Ziemann, S. Ulrich and H. Ehrardt, Diamond Relat. Mater., 1997, 6, 621.
[9] H. Hofsäss, H. Feldermann, M. Sebastian, C. Ronning, Phys. Rev. B 1997, 55 (19), 13230.
[10] C.A. Davis, Thin Solid Films 1993, 226, 30.
[11] H. Windischmann, J. Appl. Phys. 1987, 62(5), 1800 .
[12] M.-A. Djouadi, V. Mortet, S. Khandozhko, P.Y. Jouan, G. Nouet, surf. Coat. Technol. 2001, 142-144, 899.
[13] M. A. Djouadi, O. Banakh, A. Soltani, R. Sanjines, F. Levy, Thin Solid Films 2001, 398-399, 205.

[14] M. Ben El Mekki, M.-A. Djouadi, V. Mortet, E. Guiot, G. Nouet, N. Mestres, Thin Solid Films 1999, 355-365, 89.

Figure captions :
Fig. 1. SEM observation (a) and TEM microstructure (b) of the Zr-B-N coating
Fig. 2. XRD patterns of ZrBN films prepared under 12 sccm nitrogen flow as function of the bias
voltage (a) as function of the flow of nitrogen (b) (bias voltage = -100 V)
Fig. 3. IR spectra for ZrBN films as function as nitrogen percentage (a) and bias voltage (b)
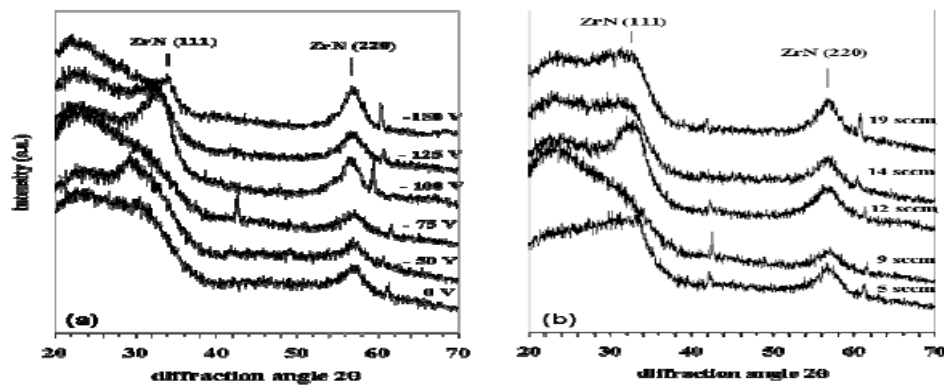**Fig. 4.** Compressive stress of ZrBN films vs nitrogen flow (a) and substrate bias voltage (b)
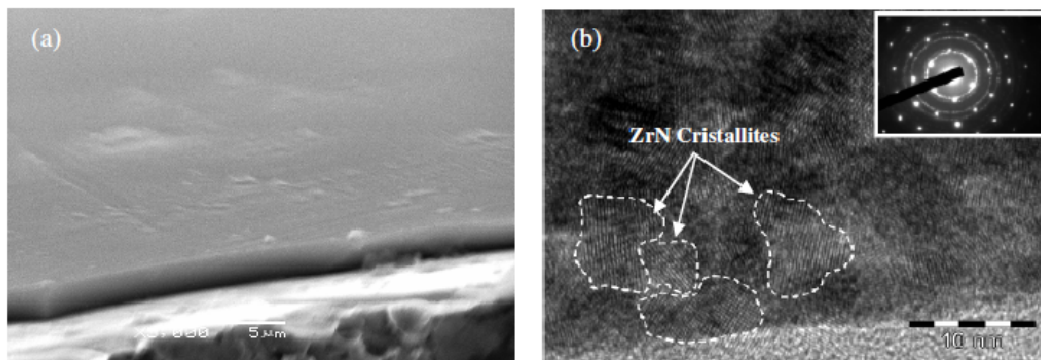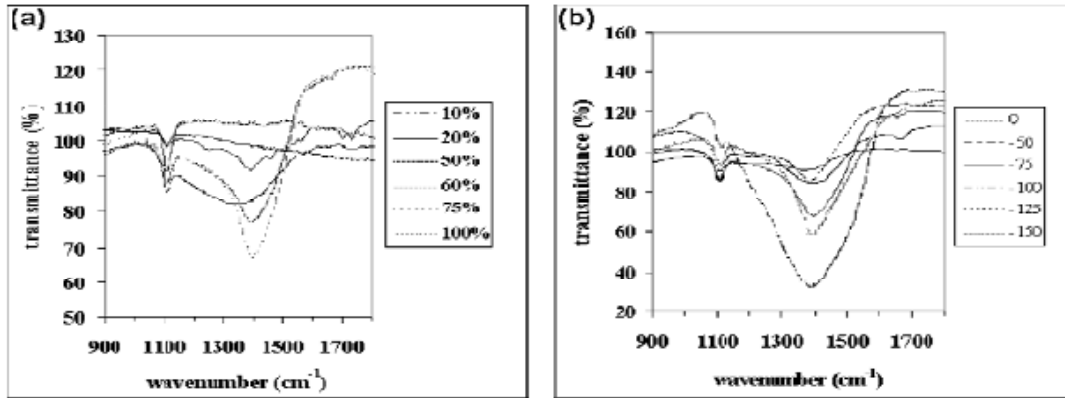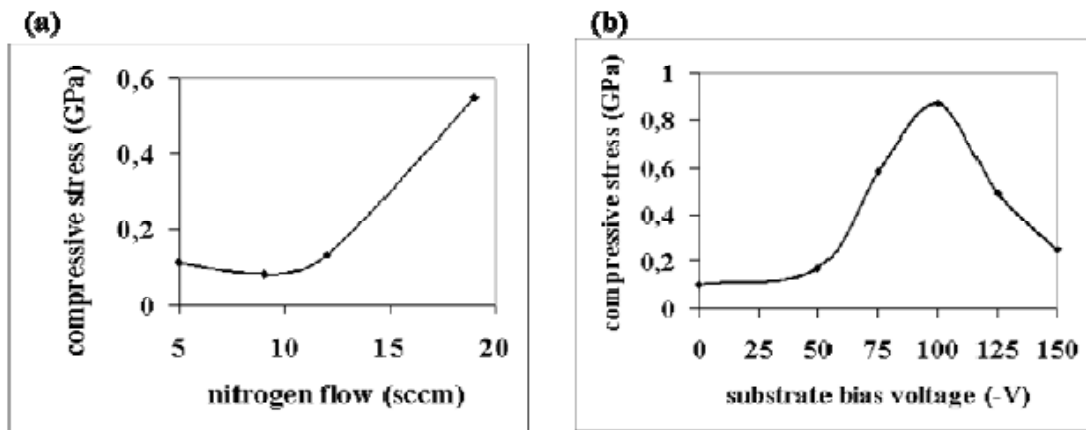

Figure 1

Figure 2

Figure 3

Figure 4

278