Thin Solid Films 518 (2009) 77–83

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Structural and mechanical characterization of $BC_xN_y$ thin films deposited by pulsed reactive magnetron sputtering

Matthias Krause [a,*], Laurent Bedel [b], Anthony Taupeau [b], Ulrich Kreissig [a], Frans Munnik [a], Gintautas Abrasonis [a], Andreas Kolitsch [a], György Radnoczi [c], Zsolt Czigány [c], Annick Vanhulsel [d]

[a] Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, POB 510119, 01314 Dresden, Germany
[b] CEA Grenoble, DRT/LITEN/DTNM/LTS, 17 rue des martyrs 38054 Grenoble cedex 9, France
[c] Research Institute for Technical, Physics and Materials Science, Hungarian Academy of Sciences, 1121 Budapest XII., Konkoly-Thege u. 29-33, Hungary
[d] VITO-Materials Technology, Boeretang 200, B-2400 Mol, Belgium

ARTICLE INFO

*Article history:*
Received 22 January 2009
Received in revised form 12 June 2009
Accepted 16 June 2009
Available online 24 June 2009

*Keywords:*
$BC_xN_y$
Thin films
Hard coatings
Magnetron sputtering
Spectroscopy
Structural properties
Mechanical properties

ABSTRACT

$BC_xN_y$ thin films deposited at 250 °C by pulsed reactive magnetron sputtering of a $B_4C$ target in an $Ar/N_2$ plasma were studied by elastic recoil detection analysis, Fourier transform infrared, Raman, and photoelectron spectroscopy, electron microscopy, and nanoindentation. In the concentration range of 6% to 100% $N_2$ in the sputter plasma the segregation into nanocrystalline hexagonal boron nitride and amorphous $sp^2$ carbon is the dominant process during the film growth. The stoichiometric ratio and structural details of the major phases depend on the $N_2$ concentration in the plasma and have significant influence on the Young's modulus and the elastic recovery of the $BC_xN_y$ thin films.



## 1. Introduction

Hard coatings of diamond like carbon and carbon nitride ($CN_x$) have been widely used due to their exceptional tribological properties [1–5]. However, their thermal stability is limited to 300 °C [2,6,7]. $B_xC_yN_z$ coatings are considered as promising alternative since their similar mechanical properties like a hardness of 15–20 GPa and an elastic modulus of 150–200 GPa are combined with a significantly better thermal stability of up to 900 °C [8]. Several publications present the structural and mechanical properties of $B_xC_yN_z$ thin films obtained by different coating processes, such as ion beam assisted deposition [8–11], plasma enhanced chemical vapour deposition [12], dual ion beam sputtering [13] and magnetron sputtering (MS) [14–24]. Using MS, amorphous [14,19] and fullerene-like [20,21] $B_xC_yN_z$ structures have been obtained. Low coefficients of friction of around 0.1 to 0.2 are reported for amorphous films [17,22]. The films with a fullerene-like structure are of particular importance since they exhibit a high elastic recovery of ≈ 80%. The fullerene-like structure $B_xC_yN_z$ could be obtained in a large composition range ($0<x<53$, $15<y<62$, $24<z<50$ at.%) provided that the deposition temperature was not lower than ~200 °C [20]. It is characterized by the presence of basal graphene or BN planes with a certain degree of curvature and cross-linking. So far, the microstructure was mainly analyzed by high resolution transmission electron microscopy (HRTEM) and is described as "fullerene-like h-BN:C" by Johansson et al. [21]. The large majority of publications reported either the structural or the mechanical properties, while studies presenting the comprehensive structural analysis and mechanical characterization of $B_xC_yN_z$ thin films are scarce [18].

In this work, structural and mechanical properties of $BC_xN_y$ thin films deposited at 250 °C by pulsed reactive magnetron sputtering of a $B_4C$ target in an $Ar/N_2$ plasma are investigated. The elemental composition was determined by elastic recoil detection analysis (ERDA). The morphology was studied by field emission gun-scanning electron microscopy (FEG-SEM) and HRTEM. The chemical structure of the coatings was analyzed by Fourier transform infrared (FTIR), Raman, and X-ray photoelectron spectroscopy (XPS). Nanoindentation was

* Corresponding author. Tel.: +49 351 260 3578; fax: +49 351 260 3285.
*E-mail addresses:* matthias.krause@fzd.de (M. Krause), laurent.bedel@cea.fr (L. Bedel), u.kreissig@fzd.de (U. Kreissig), f.munnik@fzd.de (F. Munnik), g.abrasonis@fzd.de (G. Abrasonis), a.kolitsch@fzd.de (A. Kolitsch), radnoczi@mfa.kfki.hu (G. Radnoczi), czigany@mfa.kfki.hu (Z. Czigány), annick.vanhulsel@vito.be (A. Vanhulsel).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.06.030

used to determine the elastic properties and the hardness. Correlations between structural and mechanical properties are revealed based on the comprehensive characterization.

## 2. Experimental details

### 2.1. Coating deposition

The $BC_xN_y$ coatings were deposited by pulsed reactive magnetron sputtering at a constant pressure of about 0.5 Pa. The 3 inch targets of $B_4C$ (99.9% purity) were located at 8 cm distance from the substrate holder, heated to 250 °C. An $Ar/N_2$ mixture was used as sputtering gas and the total gas flow was kept constant at 70 sccm. The substrates of Si (100) were cleaned ultrasonically in acetone for 10 min before they were mounted in the sputter chamber. The base pressure before the deposition was below $10^{-4}$ Pa. Subsequently, the substrates were cleaned for 20 min in an argon plasma (−500 V bias voltage) to improve the adhesion, and finally the target was sputter cleaned for 10 min at an argon pressure of 0.5 Pa. The coating deposition time was about 90 min, the pulse frequency was set at 50 kHz, and the reverse voltage was 15% with a reverse time of 5 µs.

### 2.2. Characterisation of the thin films

The morphology of the films was investigated using FEG-SEM (LEO 1530). The thickness of all films was about 1 µm as determined by cross-section SEM observations and calo test. The atomic composition of 8 selected $BC_xN_y$ films was measured by ERDA. The measurements were performed with 35 MeV $Cl^{7+}$ ions impinging at an angle of 15° relative to the surface. The scattered ions and the recoils were detected with a Bragg ionisation chamber located at a scattering angle of 30°. Additionally, a standard Si detector was placed at an angle of 38° for hydrogen detection. In this case, an aluminium foil was employed in front of the detector to absorb heavier recoils and backscattered $Cl^{7+}$ ions.

The chemical structure of the $BC_xN_y$ coatings was analyzed by FTIR spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The FTIR spectra were measured by a Thermo-Nicolet Nexus spectrometer operating in transmission mode. Spectra were recorded in the wave number range of 4000 to 400 $cm^{-1}$ with a resolution of 4 $cm^{-1}$ and by averaging 400 accumulations. They were analyzed after the subtraction of the Si substrate background and the conversion into absorbance units. Raman spectra were recorded using a Labram HR 800 spectrometer (Jobin Yvon, France) coupled to a BX-40 microscope with a 50 fold magnifying long working distance objective (Olympus, Germany). For excitation a frequency doubled Nd:YAG laser with an emission wavelength of 532 nm was used. The laser power on the sample was 2 mW. The spectral resolution was set to 4 $cm^{-1}$. The scattered light was collected in a 180° back scattering geometry. No sample degradation was detected under the given conditions. The Raman spectra were measured at three different sample areas and averaged for data processing. XPS spectra were recorded by a Theta-probe system from Thermo Electron Co., using monochromatic Al Kα irradiation (1486.6 eV). Spectra were obtained at 100 W and a spot size of 400 µm diameter. To exclude contaminations by other elements, survey spectra from 0 eV to 1000 eV were recorded at 300 eV pass energy and 1 eV step size. Subsequently, the photoemission from the carbon 1s and the nitrogen 1s states were recorded with high resolution using 100 eV energy pass and 0.1 eV step size. The measurements were performed at a take-off angle of 25° to the surface normal. To compensate specimen charging, the energy scale was calibrated in reference to the $sp^2$ carbon peak at 285 eV.

Specimen for cross-sectional TEM investigations were prepared by gluing slices of the samples film to film into the window of a Ti disk. The specimens were grounded by mechanical thinning to ~50 µm and dimpled from both sides to the thickness of ~16 µm in the middle. The final polishing was performed with ¼ µm diamond paste. Finally, the disks were thinned to electron transparency by ion beam milling with a 10 keV $Ar^+$ ion beam at an angle of incidence of 4° with respect to the milled surface. In the last step of the procedure the ion energy was decreased to 3 keV to minimize surface damage. The sample preparation procedure is described in detail elsewhere [25]. TEM investigations were carried out on a Philips CM20 transmission electron microscope operated at 200 kV with 2.8 Å resolution.

The Young's modulus, nanohardness, and the elastic recovery of the films were determined by nanoindentation (CSM Instruments) using a Berkovich indenter at 3 mN load. The Oliver and Pharr method (O&P) [26] and the Bull method [27] were used to determine the mechanical properties. The Bull method gave a lower standard deviation for the films of this study than the Oliver and Pharr method: i) (±1 GPa) for the hardness compared to (±5 GPa), and ii) (±10 GPa) for the Young's modulus instead of (±16 GPa). The advantage of the Bull method is that the contact point is not used to determine the mechanical properties. Therefore it has been used for the evaluation of the mechanical properties of the $BC_xN_y$ films of this study. Only for comparison, the average value obtained by the O&P method is also given.

## 3. Results

### 3.1. Film composition

Using different $N_2$ concentrations in the $Ar/N_2$ sputtering plasma, a systematic dependence of the film composition on the $N_2$ concentration in the reactor plasma is found. The atomic composition of 8 selected films is presented in Table 1 and the ternary B–C–N diagram in Fig. 1. Sputtering of the $B_4C$ target in an Ar plasma gives a film with almost the same composition as the target. The small nitrogen content of ~3 at.% is due to the use of nitrogen to refill the vacuum chamber after the deposition. Despite the significant variation of the $Ar/N_2$ ratio in the sputtering gas, all the coatings produced with $N_2$ in the gas have compositions situated in the same area of the ternary B–C–N phase diagram, centering at a B/N ratio of approximately 1/1. Apparently, this regime plays the dominant role in the formation of the coatings.

Carbon represents a minor fraction in the $BC_xN_y$ films. The B/C ratio shows a systematic dependence on the $N_2$ ratio in the sputtering gas. For nitrogen concentrations from 6% to 20%, B/C ratios of ~3/1 are obtained. Increasing the nitrogen concentration to 29%, a B/C ratio of 4/1 is found, until a maximum B/C ratio of ~6/1 is obtained for a content of 50% $N_2$ in the sputtering plasma. Further increase of the nitrogen concentration reduces the B/C ratio to ~4/1 and ~2.4/1 for $N_2$ of 70% and 100%, respectively. The results indicate a preferred formation of a few principal film compositions rather than that of random element combinations. Within a given integer B/C ratio a

**Table 1**
Chemical composition of selected $BC_xN_y$ films as a function of the $N_2$ concentration in the sputter gas.

| $N_2$ concentration in the sputter gas | Chemical composition of $BC_xN_y$ films |
|---|---|
| 0% | $BC_{0.22}N_{0.04}$ |
| 6% | $BC_{0.33}N_{0.86}$ |
| 11% | $BC_{0.32}N$ |
| 20% | $BC_{0.35}N_{1.07}$ |
| 29% | $BC_{0.24}N_{1.02}$ |
| 50% | $BC_{0.18}N_{1.06}$ |
| 70% | $BC_{0.27}N_{1.07}$ |
| 100% | $BC_{0.41}N_{1.24}$ |

The data were obtained by ERDA. The $BC_xN_y$ film compositions are given relative to a boron content of 1.0. Hydrogen (~2.7 at.%) and oxygen (~1.2 at.%) impurities due to adsorbed water were disregarded.