New Quaternary Si-B-C-N Films
Prepared by Reactive Magnetron Sputtering

J. Vlcek, S. Potocky, J. Houska, P. Zeman, V. Perina[*] and Y. Setsuhara[**]

Department of Physics, University of West Bohemia, Univerzitni 22, 306 14 Plzen, Czech Republic
Fax: +420-377632202, e-mail: vlcek@kfy.zcu.cz
*Nuclear Physics Institute, Academy of Sciences of the Czech Republic, 250 68 Rez near Prague, Czech Republic
Fax: +420-220941130, e-mail: perina@ujf.cas.cz
**Joining and Welding Research Institute, Osaka University, 11 -1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
Fax: +81-668798641, e-mail: setsuhara@jwri.osaka-u.ac.jp

Novel quaternary Si-B-C-N films were fabricated using dc magnetron co-sputtering of silicon, boron and carbon from a single C-Si-B or B_4C-Si target in nitrogen-argon gas mixtures at substrate temperatures of 180-350 °C. The films, typically 2-5 μm thick, were found to be amorphous in nanostructure with a low compressive stress (around 1 GPa) and good adhesion to substrates. They exhibited high hardness (up to 45 GPa) and elastic recovery (up to 85%), and extremely high oxidation resistance in air at elevated temperatures (up to a 1350 °C substrate limit).

Key words: Si-B-C-N, Magnetron co-sputtering, Mechanical properties, High-temperature stability, Nanostructure

1. INTRODUCTION

During recent years precursor-derived Si-B-C-N ceramics, produced at elevated temperatures (1000-1400 °C), have become of topical interest due to their extraordinary high-temperature stability (see, for example, Refs. 1 and 2). The novel quaternary Si-B-C-N materials attract great attention also due to their potential applications in coating technologies and micro-electronics. They can provide a unique combination of properties, such as extremely high temperature stability and oxidation resistance, low thermal coefficient of expansion, low thermal conductivity, high hardness, high creep resistance even at elevated temperatures, promising optical and electronic properties, reduced film stresses and good adherence to substrates [3].

In our recent work [3], reactive dc magnetron co-sputtering using a composed C-Si-B target in nitrogen-argon gas mixtures at the substrate temperature of 350 °C was proved to be a suitable technique for a reproducible deposition of hard amorphous Si-B-C-N films with a high-temperature oxidation resistance in air (up to a 1350 °C substrate limit). A particular attention was paid to the influence of ion bombardment characteristics (mainly the kinetic energy and total flux of ions bombarding the growing films) and the quantities derived from them (the ion energy per deposited atom and ion-to-film-forming particles flux-ratio) on the film properties. In this paper, the effect of the negative substrate bias voltage on mechanical properties of the Si-B-C-N films is shown, together with their very high temperature stability and oxidation resistance in air at elevated temperatures. In addition, a beneficial role of silicon in reducing the compressive stress in the films will be presented.

2. EXPERIMENTAL DETAILS

A Balzers BAS 450 PM Cryo sputtering system was used with a planar rectangular unbalanced magnetron (127×254 mm^2) and a modified circular substrate holder (125 mm in diameter), see Refs. 4 and 5. The Si-B-C-N films were deposited on p-type Si (100) substrate using dc magnetron co-sputtering of silicon, boron and carbon from composed targets in nitrogen-argon gas mixtures. A composed C-Si-B target [3], formed by a high-purity graphite plate (thickness 6 mm) overlapped by p-type Si and B stripes with a fixed 20% boron fraction in the target erosion area, and B_4C-Si target, formed by a B_4C plate overlapped by the Si stripes in the erosion area, were used for our experiments. The total pressure of nitrogen-argon gas mixtures was p = 0.5 Pa at a constant gas flow approximately 25 sccm. The target-to-substrate distance was 100 mm. The discharge current on the magnetron target was held constant at I_m = 1 A, and the negative substrate bias voltage, U_b, induced by an rf generator operating at a frequency of 13.56 MHz, was varied from a floating potential U_f = −15 V to U_b = −500 V. The substrate temperature was adjusted at T_s = 350 °C by an Ohmic heater or it was in the range from 180 to 250 °C without the heater.

The film thickness (typically between 2 and 5 μm) and a bending of the substrate after deposition of the film, from which a residual macrostress was determined using the original Stoney's formula [6], were measured by profilometry (Dektak 8 Stylus Profiler, Veeco). X-ray diffraction analysis (Dron IV Diffractometer upgraded by Seifert GmbH) indicated amorphous structure of films. The elemental composition of the films was determined by Rutherford backscattering spectrometry and elastic recoil detection (see the content of hydrogen) methods using a Van de Graaf generator with a linear electrostatic accelerator [3]. Film hardness, effective Young's modulus, $E/(1-v^2)$, where E and v are the
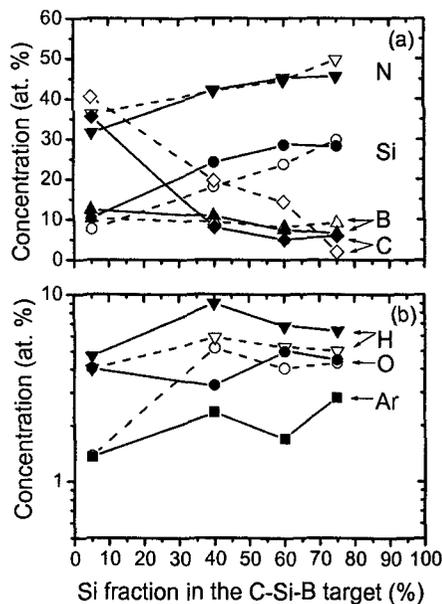
Fig. 1. Elemental composition of films prepared in a 50% N_2 + 50% Ar gas mixture at various silicon fractions in the C-Si-B target erosion area (with a fixed 20% boron fraction) for U_b = -500 V and T_s = 350 °C (full symbols), and U_s = U_f = -15 to -38 V and T_s = 180 -190 °C (empty symbols).

Young's modulus and the Poisson's ratio, respectively, and elastic recovery were determined using an ultra-microindenter (Fischerscope H–100 B) which automatically records the depth of indentation of a Vickers pyramidal tip, while increasing the applied load up to a preset maximum (30 and 50 mN in the present work). The nanostructure of films was characterized by means of high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) on cross-section foils using a TOPCN EM-002B operating at 200 kV. The high-temperature oxidation resistance of films was measured in a pure air with a flow rate of 1l/h using a symmetrical high-resolution Setaram thermogravimetric system TAG 2400. The heating rate was 10 °C/min and the heating temperature was ranging from the room temperature to 1350 °C (the limit for Si substrate).

3. RESULTS AND DISCUSSION

3.1 Elemental composition of films

The effect of the C-Si-B target composition on elemental composition of the Si-B-C-N films is presented in Fig. 1 for a fixed nitrogen-argon gas mixture and two different choices of the U_b and T_s values. In case of U_b = -500 V and T_s = 350 °C we were interested in a role played by ion bombardment and thermal desorption effects during film growth. When the substrate was on a floating potential and T_s = 180-190 °C, we attempted to prepare high-quality Si-B-C-N films under very simple experimental conditions, i.e., without the rf-induced substrate bias and Ohmic heater. As is shown in Fig. 1(a), the increasing silicon fraction in the target erosion area from 5 to 75% results in a rising incorporation of silicon (from 8 to 30 at. %) and nitrogen (from 32 to 50 at. %) into the films, while the
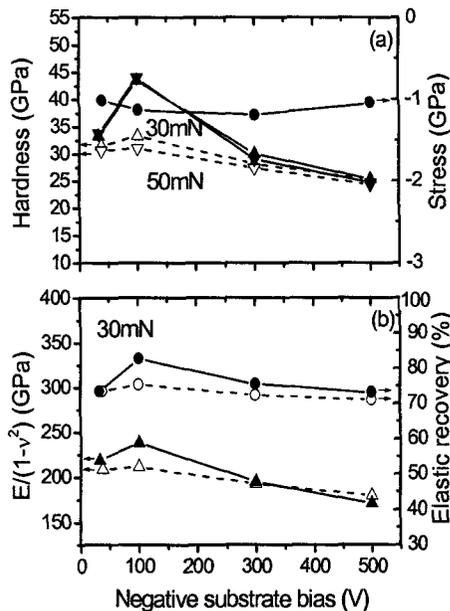
Fig. 2. Hardness and compressive stress (a), and effective Young's modulus, $E/(1-v^2)$, and elastic recovery (b) for films prepared in a 50% N_2 + 50% Ar gas mixture using a C-Si-B (20:60:20%) target at various negative substrate bias voltages and T_s = 350 °C (full symbols) or T_s = 180-250 °C (empty symbols).

carbon content decreases (from 40 to 2 at. %) at a boron content in the range from 12 to 7 at.%. The substantially lower values obtained for the C content in the films prepared at U_b = -500 V and T_s = 350 °C except for a 75% Si fraction in the target erosion area can be explained by a strong ion-induced and thermal desorption of loosely bonded C-N species from the surface of growing films. The sequential change of the Si-B-C-N films with dominant C-N and C-C bonds to the films with a dominant Si-N bond (Fig. 1) resulted in expected changes in their optical and tribological properties. The corresponding values of the extinction coefficient and the refractive index (measured at λ = 550 nm) decreased from 3×10^{-1} to 2×10^{-4} and from 2.19 to 1.85, respectively, while the friction coefficient against Al_2O_3 increased from 0.34 to 0.85. As can be seen in Fig. 1(b), typical volume concentrations of hydrogen in these films were in the range from 4 to 7 at. %, while those obtained for oxygen were 3-5 at. %.

3.2 Mechanical properties and compressive stress

The negative substrate bias voltage U_b = -100 V with the corresponding low values of the ion-to-film-forming particles flux-ratio and the ion energy per deposited atom, being approximately 0.2 and 20 eV, respectively, were found to be almost optimum for formation of hard densified amorphous Si-B-C-N materials (density around 2.4 gcm^{-3}) with strong local covalent bonds over a wide range of experimental conditions. Fig. 2 shows that the values of all examined mechanical quantities (hardness, effective Young's modulus and elastic recovery) are substantially higher at U_b = -100 V for the increased substrate temperature T_s = 350 °C, probably
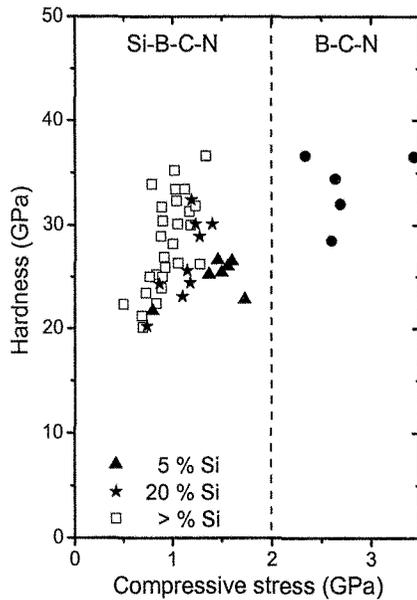
Fig. 3. Correlation between hardness and compressive stress of films prepared using various B_4C-Si targets with the denoted Si fractions (0 to 75%) in the erosion area at various N_2-Ar gas mixtures (0 to 75% Ar) and U_b values (-100 to -500 V) for T_s = 350°C.

Fig. 4. HRTEM cross-sectional image with a corresponding SAED pattern taken from a Si-B-C-N film prepared in a 25% N_2 + 75% Ar gas mixture using a C-Si-B (20:60:20%) target at U_b = -100 V and T_s = 350 °C.

due to a higher fraction of B(sp^3)–N and C(sp^3)–N bonds in the films [7]. As is seen in Fig. 2(a), there is practically no correlation between film hardness and low values (close to 1 GPa) of compressive stress in the deposited films. Another possible explanation of the presented effect of U_b values on film hardness has been suggested by results of molecular-dynamics simulations [8]. Using a liquid-quench algorithm, which allows to simulate rapid (low $|U_b|$) and slow (high $|U_b|$) cooling of the localized melt formed around sites of energetic ion impact, two types of segregation leading to a higher extrinsic hardness of the Si-B-C-N films prepared at $U_b = -100$ V were predicted. The first type are small segregated regions (most likely SiN_x), which occur as a result of random clustering in a melt and survive the rapid cooling. The second type is formation of silicon enriched zones around implanted argon atoms (1-2 at.% at $U_b = -100$ V). The energy advantage gained by surrounding Ar atoms with longer and more flexible Si-containing bonds was proposed to be a driving force for this segregation. It can also explain the ability of Si to relieve stress generated by these implanted Ar atoms [8].

A systematic decrease in the compressive stress due to a rising content of silicon in Si-B-C-N films prepared with the use of various B_4C-Si targets over a wide range of deposition conditions is shown in Fig. 3. It should be noted that the hardness of these films is lower compared to those prepared from the corresponding C-Si-B targets with a fixed 20% boron fraction and the same silicon fractions in the erosion area (see Fig. 2 and Ref. [3]).

3.3 Nanostructure of films

Fig. 4 presents an HRTEM cross-sectional image with a corresponding SAED pattern, which are typical for our Si-B-C-N films. As can be seen, the SAED pattern
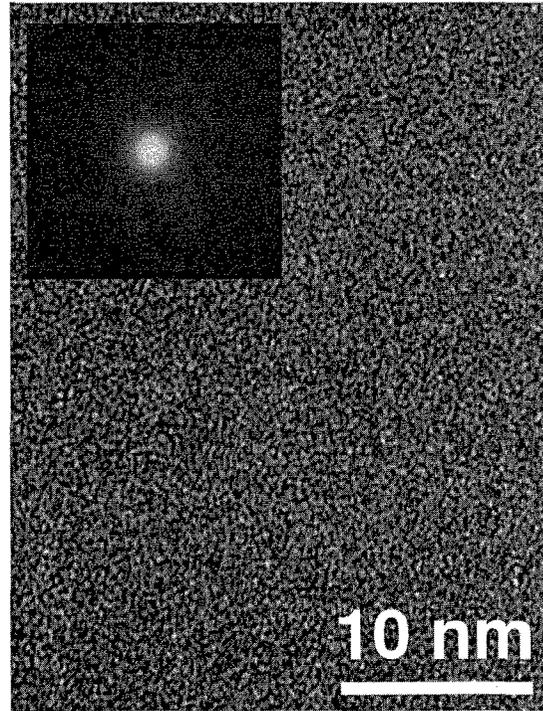
displays a diffuse halo indicating a purely amorphous nanostructure of the film. This is also confirmed by the HRTEM image, in which no obvious nanocrystallites have been identified. It should be noted that the amorphous state with a low mobility of atomic species due to strong covalent bonds is of key importance for extremely high temperature stability and oxidation resistance of these new quaternary Si-B-C-N materials [9].

3.4 High-temperature oxidation resistance

Fig. 5 shows oxidation behavior of as-deposited Si-B-C-N films in a pure air up to a 1350 °C limit. To investigate the effect of boron content in the films on their oxidation resistance the obtained results are compared with those for the Si-C-N films prepared under the same deposition conditions (5 and 40 % Si fraction in the target erosion area). In addition, the results obtained by other authors for selected hard and superhard films are also presented [10-14]. As is seen in Fig. 5, a rising incorporation of silicon and nitrogen into the Si-C-N and Si-B-C-N films at a decreasing carbon content in them leads to improved oxidation resistance of the films. This is probably caused by the ability of silicon to form a dense amorphous bonding network in the experimental situation investigated. As expected, an incorporation of boron into the films results in a systematic decrease of the measured mass changes. According to the literature, boron stabilizes amorphous state due to a reduced mobility of atomic species and prevents decomposition of Si-N bonds [9,15]. The best
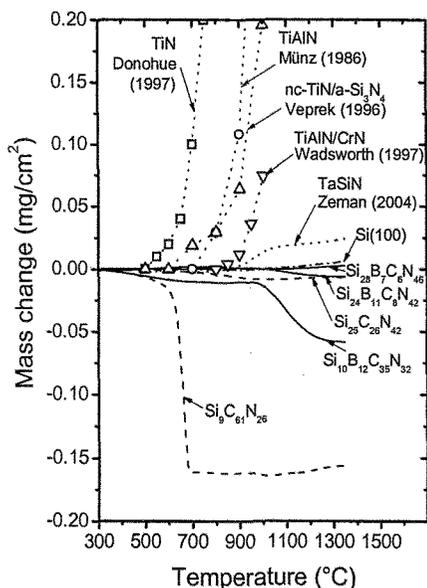
Fig. 5. Thermogravimetric analysis of as-deposited Si-B-C-N (solid curves) and Si-C-N (dashed curves) films in a pure air at a heating rate 10 °C/min. The films were prepared in a 50% N_2 + 50% Ar gas mixture at various compositions of the respective C-Si-B (with a fixed 20% boron fraction in the erosion area) and C-Si targets for U_b = -500 V and T_s = 350 °C. For a comparison, the results obtained by other authors for selected hard and superhard films are presented.

Fig. 6. Elemental composition of as-deposited films before (full symbols) and after (empty symbols) oxidization in a pure air up to 1300 °C at a heating rate 10 °C/min. The films were prepared in a 25% N_2 + 75% Ar gas mixture using a C-Si-B (20:60:20%) target at U_b = -100 V and T_s = 350°C. H_T and O_T denote concentrations of hydrogen and oxygen in the corresponding top subsurface layers (less than 50 and 150 nm, respectively), while H_V and O_V are related to volume contents.

oxidation behavior was exhibited by the Si-B-C-N film prepared at a 75% Si fraction in the target erosion area, for which almost negligible mass changes were detected even at the highest annealing temperatures (Fig. 5). After treatment, no Bragg reflections were observed in diffraction patterns taken from this film and its hardness remained practically constant (25-27 GPa). From our newest results it can be concluded that a very thin (less than 250 nm) dense surface layer (mainly composed of silicon and oxygen), which is formed during treatment, efficiently protects the Si-B-C-N films from total diffusion-controlled oxidation.

This is in agreement with Fig. 6, where a change in elemental composition of a harder (35-40 GPa) film (for which negligible mass changes were also detected in thermogravimetric analysis up to 1350 °C) after oxidization in a pure air up to 1300 °C is shown. Let us note that the volume concentrations of hydrogen and oxygen in our newly produced Si-B-C-N films [see Fig. 6(b)] have been substantially reduced (less than 2 at. % content) due to a strong reduction in a total internal area of the vacuum chamber after a considerable simplification of its internal equipment. As is seen in Fig. 6, after treatment the content of oxygen in a top subsurface layer (less than 150 nm) was 16 at. %, the silicon content increased by 2 at. % due to diffusion from the substrate and the volume content of hydrogen in the films decreased by approximately 1 at. %.

4. CONCLUSIONS

Reactive dc magnetron co-sputtering of silicon, boron

and carbon from a single C-Si-B or B_4C-Si target in nitrogen-argon gas mixtures at substrate temperatures of 180-350 °C was used for preparation of hard (up to 45 GPa), highly elastic (elastic recovery up to 85%) Si-B-C-N films with a high-temperature oxidation resistance in air (up to a 1350 °C substrate limit). The films, typically 2-5 μm thick, were found to be amorphous in nanostructure with a low compressive stress (around 1 GPa) and good adhesion to substrates. A beneficial role of silicon in reducing the compressive stress in the films was proved and very high temperature stability of the film composition during high-temperature annealing in air up to 1300 °C was shown.

6. REFERENCES

[1] P. Gerstel, A. Muller, J. Bill and F. Aldinger, Chem. Mater., 15, 4980-4986 (2003).
[2] J. Haug, P. Lamparter, M. Weinmann and F. Aldinger, Chem. Mater., 16, 83-92 (2004).
[3] J. Vlcek, S. Potocky, J. Cizek, J. Houska, M. Kormunda, P. Zeman, V. Perina, J. Zemek, Y. Setsuhara and S. Konuma, J. Vac. Sci. Technol., A 23, 1513-1522 (2005).
[4] J. Vlcek, K. Rusnak, V. Hajek and L. Martinu, J. Appl. Phys., 86, 3646-3654 (1999).

[5] J. Vlcek, M. Kormunda, J. Cizek, Z. Soukup, V. Perina and J. Zemek, Diamond Relat. Mater., 12, 1287-1294 (2003).

[6] J. Gunnars and U. Wiklund, Mater. Sci. Eng., A 336, 7-21 (2002).

[7] M. K. Lei, Q. Li, Z. F. Zhou, I. Bello, C. S. Lee and S. T. Lee, Thin Solid Films, 389, 194-199 (2001).

[8] J. Houska, O. Warschkow, M. M. M. Bilek, D. R. McKenzie, J. Vlcek and S. Potocky, submitted to J. Phys.: Condens. Matter (2005).

[9] H. Schmidt, G. Borchardt, S. Weber, H. Scherrer, H. Baumann, A. Muller and J. Bill, J. Non-Cryst. Solids, 298, 232-240 (2002).

[10] W.-D. Munz, J. Vac. Sci. Technol., A4, 2717-2725 (1986).

[11] S. Veprek, M. Haussmann, S. Reiprich, Li Shizhi and J. Dian, Surf. Coat. Technol., 86-87, 394-401 (1996).

[12] L. A. Donohue, I. J. Smith, W.-D. Munz, I. Petrov and J. E. Greene, Surf. Coat. Technol., 94-95, 226-231 (1997).

[13] I. Wadsworth, I. J. Smith, L. A. Donohue and W.-D. Munz, Surf. Coat. Technol., 94-95, 315-321 (1997).

[14] H. Zeman, J. Musil and P. Zeman, J. Vac. Sci. Technol., A 22, 646-649 (2004).

[15] A. Muller, P. Gerstel, M. Weinmann, J. Bill and F. Aldinger, J. Eur. Ceram. Soc., 21, 2171-2177 (2001).