Superior high-temperature oxidation resistance of magnetron sputtered Hf–B–Si–C–N film

P. Zeman^{a,*}, Š. Zuzjaková^a, P. Mareš^a, R. Čerstvý^a, M. Zhang^b, J. Jiang^b, E. I. Meletis^b,
J. Vlček^a

^a *Department of Physics and NTIS - European Centre of Excellence, University of West
Bohemia, Univerzitní 8, 306 14 Plzeň, Czech Republic*

^b *Department of Materials Science and Engineering, The University of Texas at Arlington,
Arlington, 76019 TX, USA*

Abstract

A hard and optically transparent amorphous Hf₇B₂₃Si₁₇C₄N₄₅ film with a contamination level less than 4 at.%, prepared by reactive pulsed dc magnetron sputtering, was subjected to systematic investigation of high-temperature oxidation behavior in air up to 1700°C. We focus on thermogravimetric analysis of the film in air and on the evolution of the film structure, microstructure and elemental composition with an annealing temperature ranging from 1100°C to 1700°C. The film exhibits a superior oxidation resistance up to 1600°C due to a formation of a nanocomposite protective oxide layer on the surface above 1000°C. The layer consists of monoclinic and tetragonal (or orthorhombic) HfO₂ nanocrystallites surrounded by a SiO₂-based amorphous matrix, most probably containing boron. The HfO₂ nanocrystallites exhibit a gradient in size with a dense population of small (a couple of nm) crystallites next to the interface and larger but dispersed crystallites close to the surface.

Keywords: Hf–B–Si–C–N; High-temperature material; Superior oxidation resistance; Nanocomposite oxide layer; Protective coating

* Corresponding author. Tel.: +420 377 632211; fax: +420 377 632202.
E-mail address: zemanp@kfy.zcu.cz (P. Zeman).

1. Introduction

Thermal protection of surfaces of high-speed cutting tools, turbine blades and vanes, wing leading edges and nose cones of hypersonic vehicles at temperatures exceeding 1000°C, or even approaching 2000°C, in highly oxidizing environments requires new high-temperature materials resistant to heat and oxidation, and new technologies for their manufacturing. Recently, ultrahigh temperature ceramics (UHTCs) such as borides (ZrB_2 , HfB_2), carbides (TaC , ZrC , SiC), nitrides (HfN , NbN), and their composites have attracted a particular interest owing to their extremely high thermo-chemical and thermo-mechanical stability [1].

Among the most studied UHTCs, sintered ZrB_2 - SiC and HfB_2 - SiC composites have shown a superior oxidation resistance with a low and thermally stable oxidation rate between 1100°C and 1500°C [2-18]. At temperatures lower than 1100°C, the oxide scale consists mainly of a protective liquid B_2O_3 top layer and a ZrO_2 (HfO_2) underlayer containing SiC grains and pores filled by B_2O_3 . Above 1100°C, B_2O_3 starts to evaporate losing a protective function and SiC starts to oxidize. SiO_2 , as a solid product of this oxidation, reacts with a still available B_2O_3 forming a protective top layer of borosilicate glass, which also fills the pores of the ZrO_2 (HfO_2) underlayer. Since the borosilicate glass, compared to liquid B_2O_3 , has a higher viscosity, higher melting point, lower oxygen diffusivity and lower vapor pressure, this double-layer oxide scale formed on the surface is more efficient to protect the composites against a rapid oxidation at these temperatures. In addition, it has been observed that the oxidation resistance of HfB_2 -based ceramics is higher than of those based on ZrB_2 [4, 14].

In this paper, we report an excellent oxidation behavior (up to 1600°C) of a hard and optically transparent Hf-B-Si-C-N film prepared by reactive pulsed dc magnetron co-sputtering. So far, no data about such a material in a thin-film or bulk form have been published in the literature. Reactive magnetron co-sputtering is a non-equilibrium deposition technique, which allows us to prepare new advanced materials in a wide composition range with a tailored structure and architecture without the presence of dangerous gas precursors. The present study

follows up on our previous papers [19, 20], which have been focused on HfB₂-based Hf–B–Si–C films with a high hardness (up to 37 GPa), high electrical conductivity (electrical resistivity on the order of 10⁻⁶ Ω·m) and oxidation resistance in air up to 800°C. In view of the role of nitrogen in ultrahigh thermal stability of Si–B–C–N films [21-24], we incorporated nitrogen into Hf–B–Si–C films to stabilize their material structure, to limit the boron release from them and to extend their oxidation resistance to temperatures considerably exceeding 1000°C. Thermogravimetric oxidation analysis, and the evolution of the structure, microstructure and elemental composition with increasing annealing temperature are presented in this paper for a Hf–B–Si–C–N film prepared at optimized process parameters.

2. Experimental details

The Hf–B–Si–C–N film selected for high-temperature oxidation resistance investigation was deposited using reactive pulsed dc magnetron co-sputtering of hafnium, silicon, boron and carbon from a single B₄C–Hf–Si target in an argon-nitrogen mixture. The target (127×254 mm²) was formed by a B₄C plate (6 mm thick) overlapped by p-type Si and Hf stripes with fixed 65% B₄C+15% Hf+20% Si fractions in the target erosion area. The magnetron was driven by a pulsed dc power supply (Rübig MP 120) operating at a repetition frequency of 10 kHz and an average target power of 500 W in a period with a fixed 85 μs negative-voltage pulse length. The voltage pulse length of 85 μs is sufficiently short to avoid arcing at the non-conductive layer formed on the B₄C–Hf–Si target during reactive sputtering of the Hf–B–Si–C–N films in an argon–nitrogen gas mixture (for further details see Ref. [24]). The base pressure before the deposition was 3×10⁻³ Pa. The film was deposited on polished and ultrasonically pre-cleaned single-crystalline Si(100) and SiC substrates held at a floating potential under the following conditions: the N₂ fraction in the gas mixture of 20%, the total gas pressure of 0.5 Pa, the target-to-substrate distance of 100 mm and the substrate temperature of 450°C. Using the floating potential (i.e., the ability to prepare well-densified films without any substrate bias)

improves the application potential of the films due to a simplified deposition process and a decreased ion-induced compressive stress.

The high-temperature oxidation resistance of the Hf–B–Si–C–N film was investigated by thermogravimetry (TG) using a symmetrical high resolution Setaram TAG 2400 system. The TG analysis was carried out in synthetic atmospheric air flowing with a rate of 1 l/h with dynamic heating in the temperature range from room temperature up to 1700°C. The heating and cooling rates were set to 10 and 30°C/min, respectively. The substrates were coated only on one side. After subtracting the thermogravimetric signal corresponding to oxidation of the uncoated sides, the resulting thermogravimetric curve is related to the oxidation resistance of the Hf–B–Si–C–N film only.

X-ray diffraction (XRD) measurements of the structure of the as-deposited and annealed film after its cooling down to room temperature were carried out on a PANalytical X'Pert PRO diffractometer working in the modified Bragg-Brentano configuration with the ω -offset of 1.5° using Cu K α radiation ($\lambda = 0.154187$ nm). The data were collected using an ultrafast detector X'Celerator in the 2θ range of 8° – 60° with a scanning speed of 0,036°/s.

The microstructure of the annealed film was studied in cross-sections by scanning electron microscopy in a Hitachi SU-70 field-emission electron microscope (SEM) and by transmission electron microscopy (TEM) in a Hitachi H-9500 electron microscope operated at 300 kV with a point resolution of 0.18 nm. Selected-area electron diffraction patterns (SAED) and high-resolution TEM images (HRTEM) were recorded in the TEM microscope. Cross-section TEM specimens were prepared by the procedure of mechanical grinding, polishing and dimpling followed by Ar-ion milling using a Gatan model 691 precise ion polishing system.

The elemental composition of the as-deposited and annealed film was determined by Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD) methods. The contents of Hf, B, Si, C, N, O and Ar were measured by RBS, while the content of H was measured by ERD. Regarding the constitutive elements (Hf, B, Si, C, N), the maximum

measurement error is 3 at.%. Regarding other elements observed in the film, the maximum content of Zr (contamination of the Hf stripes), H, O and Ar is 1, 2, 3 and 3 at.%, respectively.

The film thickness and curvature of the Si substrate coated with the film, from which a residual macrostress was determined using the modified Stoney's formula including the biaxial modulus of the substrate, were measured by profilometry (Dektak 8 Stylus Profiler, Veeco). Hardness, elastic recovery and effective Young's modulus of the as-deposited and annealed film were determined from the load vs. displacement curves measured by a Fischerscope H100 microhardness tester with the Vickers diamond indenter at a load of 20 mN. The refractive index and extinction coefficient of the as-deposited film and the thickness of the oxide layer on the surface of the annealed film were determined by variable angle spectroscopic ellipsometry (VASE) using the J.A. Woollam Co. Inc. instrument. The measurements were performed in a range from 300 to 2000 nm using angles of incidence of 65°, 70° and 75° in reflection. The optical data were fitted using the WVASE software. The electrical resistivity of the as-deposited film was measured at room temperature by a standard four-point technique with a 1.047 mm spacing between tips. The average surface roughness, R_a , was analyzed from a randomly selected square area of $5 \times 5 \mu\text{m}^2$ by atomic force microscopy using a SmartSPM microscope (AIST-NT) with a silicon tip (nominal radius of 10 nm) in non-contact mode.

3. Results and discussion

In the following part, the results for high-temperature oxidation behavior of a magnetron sputtered Hf–B–Si–C–N film are presented and discussed. First, properties and characteristics of the as-deposited film are summarized. Then, thermogravimetric oxidation analysis up to 1700°C in air is presented (Fig. 1) and changes in the crystalline structure (Fig. 2), microstructure (Fig. 3) and elemental composition (Fig. 4) in the temperature range of 1100–1500°C are shown, and related processes are discussed.

The film investigated was selected from a series of Hf–B–Si–C–N films deposited at fixed 15% Hf and 20% Si fractions in the target erosion area and a varying N_2 fraction in argon-

nitrogen gas mixtures from 0 to 50%. Its elemental composition (in at.%) $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$, with a low (< 4 at.%) total content of Zr, H, O and Ar, corresponding to a 20% N_2 fraction in the gas mixture is a result of different sputtering yields of individual elements of the B_4C -Hf-Si target and complex reactions occurring in the argon-nitrogen plasma and on the substrate where the film grows. The film with this composition exhibited the highest oxidation resistance in air, with a negligible mass gain ($< 2 \mu\text{g}/\text{cm}^2$) at 1300°C , in the series of the Hf-B-Si-C-N films considered. In the as-deposited state, the film is characterized by an amorphous structure, a thickness of $1.4 \mu\text{m}$, a hardness of 19 GPa, a Young's modulus of 173 GPa, an elastic recovery of 72 %, a residual macrostress of -0.8 GPa and a non-measurable electrical resistivity (higher than $10^8 \Omega\cdot\text{m}$). The film is optically transparent with a refractive index of 2.05 and an extinction coefficient of 0.002 (measured at 550 nm). In addition, it has a high-quality defect-free surface ($R_a \sim 0.15$ nm) and is well-adherent to Si(100) and SiC single-crystalline substrates.

The thermogravimetric oxidation curve of the $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$ film measured from room temperature up to 1700°C in flowing air is shown in Fig. 1. As can be seen, absolutely no mass changes of the film are detected to about 1200°C . It is worthwhile to note that the scale of the vertical axis is set to show extremely low mass changes ($\mu\text{g}/\text{cm}^2$). Between 1200°C and 1600°C very small mass changes are observed. The mass increase between 1200°C and 1400°C is followed by a subsequent mass decrease. This behavior indicates that competitive processes of oxidation and evaporation (volatilization) occur in this temperature range. A further increase of the annealing temperature up to 1700°C results in a pronounced mass loss, which is associated with a disturbance of the dense structure of the film (discussed more later).

Based on these thermogravimetric data, the $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$ film was annealed in air to six selected temperatures (1100 – 1500°C with a step of 100°C and 1700°C) and after its cooling down to room temperature, XRD, SEM, TEM, HRTEM, SAED and RBS analyses were carried out with the aim to gain a detailed insight into processes occurring during annealing. For each temperature a new specimen of the film was used.

Figure 2 shows XRD patterns of the film before and after annealing to specified temperatures. As mentioned above, the as-deposited film exhibits an amorphous structure without a diffraction signal of any crystalline phases. Up to 1100°C, no changes in the structure of the amorphous film are observed. On the other hand, the annealing to 1200°C leads to a formation of monoclinic hafnia (m-HfO₂ – JCPDS Card No. 34-0104) with broad and low-intensity diffraction peaks. The positions of these peaks, however, overlap with those of tetragonal hafnia (t-HfO₂ – JCPDS Card No. 08-0342) or orthorhombic hafnia (o-HfO₂ – JCPDS Card No. 04-003-6960). Therefore the existence of these phases at 1200°C cannot be excluded by XRD. With a further increase in the annealing temperature the peak intensities increase, the peak widths decrease and a new diffraction peak at $2\theta=30.31^\circ$ appears at 1300°C. The position of this peak is very close to the positions of the t-HfO₂ and o-HfO₂ diffraction standards. The unambiguous identification is, however, complicated by an occurrence of only one peak in the XRD pattern. The presence of both of the metastable phases at room temperature is, however, possible. The high-temperature t-HfO₂ phase and the strain-induced o-HfO₂ phase can be namely stabilized by a Si addition. Fischer and Kersch carried out *ab initio* simulations and they found out that bulk t-HfO₂ becomes more stable upon Si doping (~ 6 at.%) than m-HfO₂ [25]. Moreover, the critical concentration of Si can be lowered in case of thin films (~ 10 nm) due to a lower surface energy of t-HfO₂ [26]. The same size-effect is also observed when t-ZrO₂ particles are stabilized [27]. The o-HfO₂ phase has been observed in thin films (~ 4-10 nm) if the Si concentration is even lower than corresponds to the stabilization of the t-HfO₂ phase (~ 4 mol.% SiO₂) and if a hafnia layer is mechanically confined by a capping layer [28-30]. In our case, all of these effects can take place. A slight shift of the diffraction peak at $2\theta=30.31^\circ$ to higher 2θ angles (i.e., a lower lattice spacing) than corresponds to the t-HfO₂ diffraction standard can result from a substitution of larger Hf ions (0.84 Å) by smaller Si ions (0.26 Å) in the cation sublattice, i.e., by Si doping. In addition, HfO₂ nanocrystallites are surrounded by an amorphous matrix (see Fig. 3, discussed more later), which may provide a confinement and a stabilization due to the size-effect. These facts imply that both the t-HfO₂ and

o-HfO₂ phases may be present in the oxide scale after cooling down to room temperature. Let us note that the difference in the lattice structure of the two phases leads also to their different electric polarization [29, 30]. While t-HfO₂ is antiferroelectric material, o-HfO₂ exhibits a ferroelectric behavior.

A further increase of the annealing temperature to 1500°C brings no significant changes in the structure evolution except an appearance of a very weak diffraction peak. The peak at $2\theta=21.85^\circ$ corresponds to a crystalline phase of silica, namely cristobalite (SiO₂ – JCPDS Card No. 39-1425). This proves that the oxide scale is composed not only of the phases of HfO₂ but also SiO₂ and/or SiO₂-based phases (borosilicate glass) are present. Lastly, an increase in the annealing temperature to the furnace operating maximum (1700°C) results in changes in the crystalline structure. Only diffraction peaks originating from m-HfO₂ are identified. Neither the diffraction peaks of the t-HfO₂ (o-HfO₂) nor those of the SiO₂ (SiO₂-based) phases are detected. The mass loss observed on the thermogravimetric curve at 1610°C (see Fig. 1) is probably caused by a predominant evaporation of B₂O₃ from the SiO₂-based matrix leaving cavities in the oxide scale. Consequently, the protection ability of the oxide scale is disturbed and t-HfO₂ (o-HfO₂) is not stabilized any more. SEM analysis in cross-section (not shown here) revealed that the most of the film is oxidized at 1700°C and after cooling down to room temperature it is predominantly composed of glassy-like SiO₂ (not detected by XRD) and m-HfO₂. In some cases we detected also a trace amount of the HfSiO₄ phase.

In order to obtain a more complete picture of the microstructure evolution with an increasing annealing temperature, TEM, HRTEM and SAED analyses in cross-sections were carried out for selected temperatures (1100°C, 1200°C and 1300°C on the Si substrates, and 1400°C and 1500°C on the SiC substrates). Cross-section TEM images for 1200°C and 1500°C are shown in Fig. 3a and b. As can be seen, for both the annealing temperatures the microstructure is characterized by a double layer structure comprising the original as-deposited film and a nanocomposite oxide layer on the top with HfO₂ crystallites embedded in a rather amorphous SiO₂-based matrix. A similar microstructure is also observed for other annealing temperatures

investigated. The only difference is the thickness of the oxide layer which varies with the annealing temperature, see Table 1. The thickness of the oxide layer is only 45 nm at 1100°C and it gradually grows to 545 nm at 1500°C. The HfO₂ crystallites exhibit a gradient in size with a dense population of small (a couple of nm) crystallites next to the interface and larger but dispersed crystallites close to the surface. For all the annealing temperatures, the size of the crystallites near the film/oxide interface ranges from 3 to 8 nm but considerably differs close to the surface. In case of the film annealed to 1200°C the crystallite size reaches up to about 20 nm while in case of the film annealed to 1500°C up to about 55 nm. As the film is exposed to a high temperature in air, oxygen diffuses through the oxide layer to the film/oxide interface, reacts with Hf atoms forming a dense population of HfO₂ nuclei near this interface. As the annealing temperature increases, the HfO₂ crystallites coarsen approaching the surface and producing the observed size gradient microstructure. Coarsening of the HfO₂ crystallites is, however, limited by the surrounding amorphous matrix, which is formed by oxidation of Si and B atoms at the same interface. Since B₂O₃ evaporates in the temperature range investigated as well, the amorphous matrix is suggested to be called SiO₂-based. Other gaseous species such as carbon oxides and nitrogen molecules are also released from the film during oxidation.

Figure 3c and d shows a SAED pattern and a HRTEM image taken from the oxide layer after the annealing to 1500°C, respectively. Both are in very good agreement with the XRD results (see Fig. 2) corroborating the coexistence of m-HfO₂ and t-HfO₂ (o-HfO₂). Diffraction ring 1, 2, 3, 4 and 5 in Fig. 3c has a lattice spacing of 3.67 Å, 2.95 Å, 2.54 Å, (2.12 Å/2.02 Å), (1.84 Å/1.82 Å), respectively. Diffraction rings 1, 2 and 3 can be indexed as m-HfO₂ (011), t-HfO₂ (101) or o-HfO₂ (111) and t-HfO₂ (200) or o-HfO₂ (020), respectively. Diffraction ring 4 corresponds to an assemblage of rings t-HfO₂ (112) or o-HfO₂ (121) and m-HfO₂ (112), while diffraction ring 5 corresponds to an assemblage of m-HfO₂ (022) and t-HfO₂ (220) or o-HfO₂ (022). Figure 3d shows m-HfO₂ and t-HfO₂ (o-HfO₂) nanocrystallites in a high resolution mode near the film/oxide interface shown in Fig. 3b. The nanocrystallites are basically identified to have either the m-HfO₂ or t-HfO₂ (o-HfO₂) structure. The lattice fringes in the

nanocrystallite marked by A have a spacing of 2.60 Å, which corresponds to m-HfO₂ (020) (space group P21/c, a=5.12 Å, b=5.18 Å, c=5.25 Å and β=98°) or t-HfO₂ (002) (space group P42/nmc, a=5.14 Å, c=5.25 Å). The lattice spacing of the lattice fringes in nanoparticles B and D is about 2.54 Å, which can be determined to be either m-HfO₂ (200) or t-HfO₂ (200) or o-HfO₂ (020) (space group Pbcm, a=5.00 Å, b=5.06 Å, c=5.22 Å). The lattice fringes of nanoparticles C, E and F have a spacing of ~2.93 Å, which corresponds to t-HfO₂ (101) or o-HfO₂ (111). The lattice fringes in nanoparticle G have a spacing of ~3.60 Å, which can be identified as m-HfO₂ (110). A more detailed study focused on an unambiguous identification of metastable HfO₂ phases by HRTEM is in progress.

The fact that the very compact and dense nanocomposite oxide layer provides an efficient diffusion barrier against severe oxidation at temperatures up to 1500°C is demonstrated by Fig. 4. The figure shows a dependence of the elemental composition of the Hf₇B₂₃Si₁₇C₄N₄₅ film underneath the oxide layer on the annealing temperature. It is seen that the nitrogen and boron relative contents slightly decrease above 1100°C while Si and C relative contents slightly increase. Hafnium relative content remains constant. All the changes in the atomic concentrations are, however, within the accuracy of the RBS method. Hence, the thermal stability of the elemental composition of the film is very high. The measurement of the elemental composition of the oxide layer is more complicated and is still being under investigation.

Table 1 summarizes the values of the oxide layer thickness measured by TEM and VASE and of the hardness as a function of the annealing temperature. There is very good agreement between the oxide layer thickness measured by the two methods for all the annealing temperatures. It is obvious that the hardness decreases as the oxide layer thickness increases. This indicates that the nanocomposite oxide layer possesses a lower hardness than the Hf–B–Si–C–N film.

4. Conclusions

The hard and optically transparent $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$ material was proven to have a superior high-temperature oxidation resistance in air at temperatures considerably exceeding 1000°C . High-resolution thermogravimetric analysis showed no mass changes to about 1200°C and only very low mass changes ($\pm 2 \mu\text{g}/\text{cm}^2$) up to 1600°C . In this temperature range, the amorphous structure and elemental composition of the film are efficiently protected by a single diffusion barrier formed by an oxide layer on the film surface above 1000°C . The thickness of the layer is 45 nm at 1100°C and 545 nm at 1500°C . The layer has a nanocomposite structure consisting of monoclinic and tetragonal (or orthorhombic) HfO_2 nanocrystallites surrounded by a SiO_2 -based amorphous matrix, most probably containing boron as B_2O_3 (borosilicate glass). The HfO_2 nanocrystallites grow in size from the film/oxide interface towards the surface.

The results suggest that optimized Hf–B–Si–C–N films might be used as efficient high-temperature protective coatings of electronic and optical elements, and sensors in severe oxidation environments.

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Tables

Table 1
Thickness of the nanocomposite oxide layer formed on the surface of the annealed film,
measured by TEM and VASE, along with the values of the hardness.

Annealing temperature (°C)	as-dep.	1100	1200	1300	1400	1500
TEM thickness (nm)	-	45	89	190	300	544
VASE thickness (nm)	-	46	89	196	316	561
Hardness (GPa)	19	19	18	15	11	10

Figure captions

Fig 1. Thermogravimetric oxidation curve of the $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$ film measured in air at a heating rate of $10^\circ\text{C}/\text{min}$.

Fig 2. XRD patterns taken from the $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$ film before and after annealing in air to the temperatures of 1100 - 1700°C .

Fig 3. Cross-section TEM images of (a) the $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$ film on the Si substrate annealed in air to 1200°C and (b) the $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$ film on the SiC substrate annealed in air to 1500°C . (c) SAED pattern and (d) cross-section HRTEM image of the oxide surface layer near the film/oxide interface in the image (b). The diffraction rings 1-5 in (c) and the nanocrystallites A-G in (d) are identified in the text.

Fig. 4. Elemental composition of the $\text{Hf}_7\text{B}_{23}\text{Si}_{17}\text{C}_4\text{N}_{45}$ film before (deposited at 450°C) and after annealing in air to various temperatures (1100 - 1500°C). The constitutive elements (Hf, B, Si, C, N) after annealing are measured with the maximum error of 3 at.%. Regarding other elements observed in the film, the maximum content of Zr (contamination of the Hf stripes), H, O and Ar is 1, 2, 3 and 3 at.%, respectively.

Figure1

Figure2

Figure3

Figure4