Hard nanocrystalline Zr–B–C–N films with high electrical conductivity prepared by pulsed magnetron sputtering

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ABSTRACT

Zr–B–C–N films were deposited on silicon and glass substrates using pulsed magnetron co-sputtering of a single B_4C–Zr target (at 15% or 45% of zirconium in the target erosion area) in nitrogen–argon gas mixtures. A planar unbalanced magnetron was driven by a pulsed dc power supply operating at a repetition frequency of 10 kHz with a fixed 85% duty cycle. The total pressure was 0.5 Pa and the substrate temperature was adjusted to 450 °C during the depositions on the substrates at a floating potential. High-quality defect-free films, 3.5 to 4.1 μm thick, with smooth surfaces (the average roughness $R_a \leq 4$ nm) and good adhesion to substrates at low compressive stresses (less than 0.9 GPa) were produced. Hard (37 GPa) nanocolumnar ZrB_2-type films of the $Zr_{25}B_{57}C_{14}N_3$ composition (in at.% without 1 at.% of hydrogen) with a very low compressive stress (0.4 GPa), high electrical conductivity (electrical resistivity of 2.3×10^{-6} Ωm) and high oxidation resistance in air up to 650 °C were prepared in pure argon at a 15% Zr fraction in the target erosion area. Hard (37 GPa) nanocomposite $Zr_{41}B_{30}C_8N_{20}$ films with a low compressive stress (0.6 GPa), even higher electrical conductivity (electrical resistivity of 1.7×10^{-6} Ωm) and high oxidation resistance in air up to 550 °C were deposited in a 5% $N_2 + 95\%$ Ar gas mixture at a 45% Zr fraction in the target erosion area. Increasing the N_2 fraction ($>5\%$) in the gas mixture resulted in a significant decrease of the film hardness and in a rapid rise in their electrical resistivity and oxidation resistance in air at elevated temperatures due to a growing volume fraction of an amorphous phase with a high content of nitrogen (up to 52 at.%) in the materials.

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1. Introduction

Nitrides, borides and carbides of transition metals are well known for their high hardness and wear resistance, which give rise to various applications. The development of nanostructured multicomponent films of these types over the past decade has resulted in considerable improvements of their properties in comparison to conventional single-phase films. For example, films of the Ti–B–C–N system have recently received great attention as they may combine good properties of different binary and ternary systems through a nanostructure design [1–13]. The Ti–B–C–N films may be composed of many phases, such as TiB_2, TiN, c-BN, h-BN, Ti_2N and TiC [1,7,8,11,13–17]. The understanding and control of preferred nanometer-scale multicomponents, including selected nanocrystalline and amorphous phases, during the deposition of such complex materials are the key to the fabrication of films with tailored properties.

In the literature, ZrN films with higher corrosion resistance [18,19] and lower electrical resistivity [20,21] than the TiN films with comparable mechanical properties [22–24] have been described. Moreover,

a higher oxidation resistance of ZrB_2 materials compared to TiB_2 materials was reported [25]. Zr-based carbonitride films exhibit high hardness and improved corrosion resistance and are possible candidates to be used as protective layers for medical implants [26,27]. In addition, hard Zr–B–C and Zr–B–C–N coatings with high erosion and thermal shock resistance [28], and good adhesion to substrates [29] have been reported.

In the present paper, we report on pulsed reactive magnetron sputter deposition of nanocomposite Zr–B–C–N films. The first motivation for this study came from the requirement to avoid microarcs at the target and thus to produce high-quality defect-free films needed, for example, for micro-electromechanical systems. The second motivation was to investigate the effects of the nitrogen–argon gas mixture composition on the evolution of the elemental composition, structure, and mechanical properties and electrical conductivity of the Zr–B–C–N films prepared using two different compositions of the sputtered B_4C–Zr target (15% or 45% of zirconium in the target erosion area) leading to an interesting combination of film properties. In addition, low values of the internal stresses generated in the films, their relatively high oxidation resistance in air and their smooth, defect-free surfaces will be presented. This study is the first part of an overall program that is conducted to develop new multifunctional thin-film materials in the Zr–Si–B–C–N system which would be used

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as hard protective coatings with high oxidation and corrosion resistance at elevated temperatures.

2. Experimental details

2.1. Film preparation

A Balzers BAS 450 PM sputtering system was used with a planar rectangular unbalanced magnetron (see Refs. [30,31]) and a stationary circular substrate holder (80 mm in diameter). The Zr–B–C–N films were deposited on p-type Si(100) or glass substrates using pulsed magnetron co-sputtering of zirconium, boron and carbon from a single target (127×254 mm^2) in nitrogen–argon gas mixtures. The target was formed by a B$_4$C plate (thickness of 6 mm) overlapped by Zr stripes covering 15% or 45% of 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% duty cycle. The voltage pulse duration of 85 μs is sufficiently short to avoid arcing at the non-conducting layer formed on the target during reactive sputtering. The base pressure was 3×10^{-3} Pa. The total pressure of nitrogen–argon gas mixtures was 0.5 Pa at the nitrogen fraction in the gas mixture ranging from 0% to 50% and a constant gas flow of approximately 25 sccm. The target-to-substrate distance was 100 mm. The substrate temperature was adjusted to 450 °C by an infrared heater during the depositions on the substrates at a floating potential. Our intention was to reduce a possible generation of the internal stresses in the films produced. Note that a possibility to produce films on floating substrates would also be of key importance for industrial applications.

2.2. Film characterization

The film thickness (between 3.5 and 4.1 μm) and bending of the substrate after deposition of the film, from which the residual macrostress was determined using the original Stoney's formula (see, for example, Ref. [32]), were measured by profilometry (Dektak 8 Stylus Profiler, Veeco). The elemental composition of the films was determined by the Rutherford backscattering spectrometry (RBS) and the elastic recoil detection (ERD) methods [33] as described in Ref. [30]. The contents of Zr, B, C, N, O and Ar were measured by RBS, while the content of H by ERD. The accuracy of the measurements is approximately 0.1–0.2 at.% for hydrogen and 1–2 at.% for the other elements detected.

X-ray diffraction (XRD) measurements were carried out at room temperature on a PANalytical X'Pert PRO MPD diffractometer working in the Bragg–Brentano geometry using a CuKα (40 kV, 40 mA) radiation, 0.25° divergence slit, 0.5° anti-scatter slit, 0.04 rad Soller slits, Ni filter for the CuKβ elimination and an ultrafast semiconductor detector X'Celerator. To avoid a strong reflection from the Si(100) substrate, a slightly asymmetrical diffraction geometry with an ω-offset of 1.5° was used. Samples were scanned over the 2θ-range from 8° to 60° with a scanning speed of 0.036°/s. The data were processed by a PANalytical software package HighScore Plus.

Surface morphology was determined by atomic force microscopy (AFM) using a Metris 2001A-NC Microscope (Burleigh Instruments) with a Silicon Nitride Supertip (nominal radius of 10 nm) in contact mode.

Film hardness, effective Young's modulus, $E/(1 - \upsilon^2)$, where E and υ are the Young's modulus and the Poisson's ratio, respectively, and elastic recovery defined by the W_{elast}/W_{total} ratio, where W_{elast} and W_{total} are the elastic reverse deformation work of indentation and total mechanical work of indentation, respectively, were determined using an ultramicroindenter (Fischerscope®H100VP) according to the ISO 14577–1:2002 E standard. The system automatically records the penetration depth of a Vickers diamond pyramidal tip while

increasing the applied load up to a preset maximum. The measured values of the mechanical quantities did not depend on the preset maximum load ranging from 20 to 50 mN in the present work.

Electrical resistivity of the Zr–B–C–N films, deposited on non-conductive glass substrates, was measured at room temperature by a standard four-point technique with a 1.047-mm spacing between tips.

The high-temperature oxidation resistance of the films was measured using a symmetrical high-resolution Setaram thermogravimetric system TAG 2400 in a flowing synthetic air (1 l/h) from room temperature up to 800 °C. Heating was carried out at a rate of 10 °C/min. The Si(100) substrates were coated only on one side. After subtracting the thermogravimetric signal corresponding to oxidation of their uncoated sides, the resulting thermogravimetric curves are related only to the oxidation resistance of pure Zr–B–C–N films.

3. Results and discussion

The effects of the N$_2$–Ar gas mixture composition on various characteristics of the Zr–B–C–N films (Figs. 1, 2, 4–7) are presented for two different compositions of the sputtered B$_4$C–Zr target (15% or 45% Zr fraction in the target erosion area) leading to noticeably different zirconium and boron contents in films (Fig. 1). In addition, defect-free surfaces of the selected Zr–B–C–N films exhibiting high hardness, high electrical conductivity and relatively high oxidation resistance in air are shown (Fig. 3).

3.1. Elemental composition, structure and surface morphology

Fig. 1 shows the elemental composition (in at.%) of the Zr–B–C–N films prepared from the two targets. For the 15% Zr fraction in the target erosion area (Fig. 1a), an increasing N$_2$ fraction in the gas mixture from 0% to 50% results in a rising incorporation of nitrogen (from 3 to 47–49 at.%) into the films at decreasing contents of zirconium (from 25 to 6 at.%), boron (from 57 to 34–37 at.%) and carbon (from 14 to 5 at.%) mainly due to their weakened sputtering from the target covered with reactive products (various nitrides). For the 45% Zr fraction in the target erosion area (Fig. 1b), the same increase of the N$_2$ fraction in the gas mixture leads to a similar incorporation of nitrogen (from 3 to 52 at.%) into the films at systematically higher contents
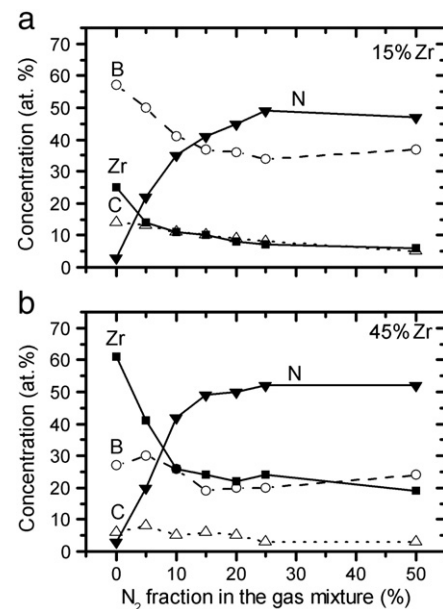

Fig. 1. Elemental composition of Zr–B–C–N films prepared using a fixed 15% (a) or 45% (b) Zr fraction in the B$_4$C–Zr target erosion area at various nitrogen fractions in the gas mixture.