Effect of Nitrogen Content on the Microstructure and Hardness of Hard Zr–B–C–N Films

Minghui Zhang¹, Jiechao Jiang¹, Jaroslav Vlček², Petr Steidl², Jiri Kohout, Radomir Cerstvy and Efstathios I. Meletis¹

¹Department of Materials Science and Engineering, The University of Texas at Arlington, Arlington, Texas 76019, USA.
²Department of Physics, University of West Bohemia, Univerzitní 22, 306 14 Plzeň, Czech Republic.

Nanostructured multicomponent films of transition metal-based carbonitrides quaternary were found to have a much wider industry-specific applications due to their outstanding properties compared to the traditional binary or ternary hard coatings [1, 2]. For example, the novel quaternary Si–B–C–N system exhibits an extraordinary high-temperature oxidation resistance and stability [3–5], while it maintains its amorphous structure at high temperatures [6]. Recently, multifunctional Zr-B-C-N films have been fabricated by pulsed reactive magnetron sputtering that can be used as hard protective coatings with high oxidation and corrosion resistance at elevated temperatures [7]. These are high-quality, defect-free films with smooth surfaces (average roughness $R_a$ ≤ 4 nm) and good adhesion to substrates.

In this work, we have employed high-resolution transmission electron microscopy, electron diffraction, X-ray photoelectron spectroscopy and nano indentation to systematically study the microstructures and mechanical properties of Zr-B-C-N films. Four films with a chemical composition of Zr$_6$B$_2$C$_6$N$_3$, Zr$_{41}$B$_{30}$C$_8$N$_{20}$, Zr$_{26}$B$_{26}$C$_6$N$_{42}$ and Zr$_{24}$B$_{19}$C$_6$N$_{49}$ were deposited on p-type Si (100) by pulsed reactive magnetron sputtering of Zr, B, and C from a single B$_4$C–Zr target in the nitrogen-argon gas mixtures with a nitrogen fraction of 0%, 5%, 10% and 15%. The B$_4$C–Zr target was prepared using a B$_4$C plate overlapped by Zr stripes covering 45% in the target erosion area. During the deposition, the substrate temperature was adjusted to 450 °C by an infrared heater on the substrates at a floating potential. The base pressure was 3×10$^{-3}$ Pa and the total pressure of argon–nitrogen gas mixtures was 0.5 Pa.

The Zr$_{6}$B$_{27}$C$_6$N$_3$ film is a composite material involving an amorphous structure surrounding face-centered cubic (fcc) B-rich Zr(B,C,N) nano-columnar structures in which the B-rich Zr(B,C,N) crystalline has a [111] preferred orientation (Fig. 1(a)). The Zr$_{41}$B$_{30}$C$_8$N$_{20}$ film consists of nano-needle structures which have a length of about 40 nm and a width of about 10 nm (Fig. 1(b)). This film was found to possess the highest hardness (36.4 GPa) and modulus (316.8 GPa). The nano-needles have a fcc structure and are composed of ZrN and/or Zr(B,N) nano-domain structures (~2 nm) that are semi-coherently joined by ZrN monolayer interfaces (Fig. 2). The Zr$_{26}$B$_{26}$C$_6$N$_{42}$ film deposited with 10% N2 fraction in the gas mixture is composed of refined crystalline ZrN nano-needle structures (~2 nm) embedded in an amorphous matrix (Fig. 1(c)). The Zr$_{24}$B$_{19}$C$_6$N$_{49}$ film has a pure amorphous-like structure (Fig. 1(d)). These results helped us to develop a better understanding of the relationship between the microstructure and the mechanical properties of the Zr-B-C-N films. The highest hardness obtained for the Zr$_{41}$B$_{30}$C$_8$N$_{20}$ film is attributed to the particular microstructure that involves Hall-Petch strengthening effects from the ZrN and/or Zr(B,N) nanograins, and interface layer strengthening from the semi-coherent Zr-N monolayer boundary. The results showed that an amorphous structure can be introduced into the films by changing the N/Zr ratio via varying the N$_2$ fraction in the N$_2$/Ar gas mixture. Formation of such an amorphous structure has a negative impact on the mechanical properties of the films.
References:

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Figure 1. Cross-section TEM image and SAED pattern (inset) of the film (a) Zr$_{61}$B$_{27}$C$_{6}$N$_{3}$, (b) Zr$_{41}$B$_{30}$C$_{8}$N$_{20}$, (c) Zr$_{26}$B$_{26}$C$_{6}$N$_{42}$ and (d) Zr$_{24}$B$_{19}$C$_{6}$N$_{49}$.

Figure 2. (a) HRTEM image of a nano needle in the Zr$_{41}$B$_{30}$C$_{8}$N$_{20}$ film showing nano domains separated by monolayer interfaces; (b) schematic illustration of atomic structure of the monolayer interface.