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Oxidation resistance of CrN/SiNx and ZrN/SiNx multilayered films deposited by magnetron sputtering technique

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Transition metal (TM) nitride films, e.g. CrN or ZrN, are widely used as hard and wear-resistant coatings in cutting tool or manufacturing industries. However, they rapidly oxidize at temperature as low as 600°C. One promising approach of both improvement of mechanical properties and resistance to high-temperature oxidation is the formation of multilayered film structures. Multilayers consisting of alternate stacking of TM nitride and SiN_x layers are characterized by very low intermixing that promotes their thermal stability and oxidation resistance.
We report here on CrN/SiN_x and ZrN/SiN_x multilayered films deposited on Si by a reactive magnetron sputtering under Ar+N_2 plasma discharges. Multilayers with various thickness ratio of elementary layers were synthesized by sequential sputtering from elemental Cr (or Zr) and Si_3N_4 targets. According to TEM and XRD analysis, the multilayered films consist of nanocrystalline (002)-oriented CrN (or ZrN) and amorphous SiN_x layers. Reducing the CrN (or ZrN) layer thickness fraction with respect to bilayer thickness leads to decrease in crystallite size and increase in the lattice parameter of CrN (or ZrN) phase due to higher compressive stress.
The oxidation resistance under air was studied using in situ XRD, in the temperature range from 400 to 950°C, as well as by WDS and SEM methods after air annealing procedure. While the reference CrN and ZrN film start to oxidize at T_{ox}=700°C and 550°C, respectively, a much higher oxidation resistance, till T_{ox}=950°C, is found for multilayered films with CrN (or ZrN) to SiN_x thickness ratio of 2 nm/5 nm and 3 nm/5 nm. We also find that CrN/SiN_x films are overall more resistant to high temperature oxidation than ZrN/SiN_x films. The influence of the interface density and chemical composition on the formation of Cr_2O_3 (or ZrO_2) oxide phases is discussed.

Keywords
Multilayer
Hard coatings