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Synthesis and characterisation of reactively r.f. magnetron sputtered Cr-Zr-O thin films

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Cr-Zr-O thin films were deposited by reactive r.f. magnetron sputtering in an argon-oxygen atmosphere in a Leybold Z 550 PVD coating machine. While keeping the r.f. target power and the substrate temperature constant, the r.f. substrate bias was varied in well-defined steps between 0 V and -200 V. In addition, a combinatorial approach for systematic variation of the Cr:Zr ratio was applied by using a segmented Cr/Zr target. This experimental approach allowed for the deposition of Cr-Zr-O films five different elemental compositions in one deposition process.
Structural analysis revealed a corundum-like nanorystalline structure, dependant on the elemental composition and bias voltage. Without substrate bias a corundum-like structure evolved up to a concentration of 12 at% Zr. Hardness values of 17 to 19 GPa were obtained. A higher Zr content leads to the formation of $(Zr,Cr)O_2$-like nanocrystalline structures and lower hardness values. The metallic:oxygen ration changes accordingly from 0.62 (Cr_2O_3 – 2:3) to 0.57 (ZrO_2 – 1:2).
Applying substrate bias, various effects on microstructure evolution were observed: the corundum-like structure could be detected up to a bias of -100 V, but only for the Cr-richest samples. The grain size decreased and the chemical analysis revealed an increasing Zr-content of about 2 at% up to 11 at%. The Cr-content decreased about 2.6 at% to 26.4 at%. Hardness could be enhanced about 20% to approximately 23 GPa. Samples with a Cr:Zr ratio ≤2 again show $(Zr,Cr)O_2$-like structures and lower hardness values. Additionally, the Cr-content decreases to almost 0 at% with increasing bias for the Zr-richest samples whereas the Zr-content in the Cr-richest samples increases to 14 at% at -200 V bias.

Keywords
PVD
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