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Investigation of microstructure and properties of magnetron sputtered Zr-Si-N thin films with different Si content

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ABSTRACT

Zr-Si-N thin films with varying silicon content were deposited by reactive magnetron sputtering in order to investigate the effect of Si content in microstructure, morphology, mechanical properties and oxidation resistance of the coatings. Characterizations were carried out using RBS, GAXRD, XPS, nanohardness, SEM and oxidation tests. Silicon content was set between 0 and 15 at.%. GAXRD results indicate peak intensity reduction and broadening increase due silicon nitride segregation, which is responsible for grain size reduction, reaching magnitudes lower than 10 nm, calculated by Scherrer. XPS confirmed the presence of compounds like ZrN and Si_3N_4. ZrN film is almost fully oxidized at 773 K, while films with high silicon content maintain ZrN grains stable at 973 K. Silicon addition to ZrN provided an increment in hardness values of 32% and also increased H^3/E^2 ratio.

1. Introduction

Transition metal nitride thin films, denominated MeN, where Me represents the elements Ti, Zr, Hf, V, Nb, Ta or Cr, possess a set of valuable properties to industrial applications, such as: high hardness, mechanical and wear resistance, thermal stability, high melting point and chemical inertness. Special attention has been given to titanium nitride (TiN), due to its high hardness and excellent tribological properties, along with chromium and zirconium nitrides, due to their corrosion and oxidation resistance derived from the formation of a protective oxide layer. Such films are frequently deposited on cutting tools aiming to improve their lifespan and provide increased productivity to machining industries [1].

Despite their excellent properties, columnar microstructure and presence of defects such as micro-cracks and porosity, characteristic features of thin films deposited by reactive magnetron sputtering (RMS), limit the field of application for MeN films. Such defects allow the direct contact between external environment and substrate, compromising the application of those coatings in high temperature situations and in the presence of aggressive fluids, which require oxidation and corrosion resistance [2–11].

Additionally, it is important to note that mechanical properties of MeN thin films are associated with a complex state of crystal lattice compression, or residual stress. Thin films deposition process commonly occurs in low temperatures ($T < 570$ K), in which atoms and molecules do not possess sufficient energy to relocate into their equilibrium state. Hence, the resulting film has its structure in a metastable phase, which tends to stabilize into a lower energy state in case necessary activation energy is provided, meaning that the excellent properties of MeN films tend to decline as a function of time and temperature [1,7,12–16].

A well-studied alternative to solve those aspects is the use of ternary systems, such as Me-Si-N, to improve characteristics of MeN coatings. Even in low quantities, the addition of a third element, in this case silicon, is able to alter chemical bonds, structure and morphology of films, consequently modifying their macroscopic properties [1,7,12–23].

Silicon addition to MeN thin films favors the formation of a biphasic microstructure, one crystalline (MeN) and the other amorphous (Si_3N_4). Amorphous phase is formed in the grain boundaries of crystalline phase, promoting a grain size reduction and resulting in a set of similar or even superior properties to those of films discussed so far.

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Microstructure, when ideally formed, is composed of grains or crystallites with reduced sizes, embedded by a thin amorphous layer of silicon nitride (Si_3N_4) segregated in grain boundaries [1,12–25]. Thus, the addition of silicon in these films causes them to move from a predominantly columnar structure to a nanocomposite one, formed by transition metal nitride nanocrystals (nc-MeN) embedded in an amorphous phase of silicon nitride (a- Si_3N_4) which improves properties of the material, such as hardness and thermal stability [26–29].

The great advantage of this type of microstructure is its permanence in equilibrium state, not being significantly affected by diffusion activated processes due to its elevated thermal stability [1,11–23]. Furthermore, formation of a nanostructure also improves other properties such as oxidation resistance. Si_3N_4 is a material that possesses great thermal stability and the fact that it involves MeN grains results in a restriction to the diffusion of oxygen inside the film, consequently enhancing oxidation resistance. Raising Si content contributes to increase the thickness of amorphous layer that separates nanograins and the potentiality of films becoming more oxidation resistant.

Particularly, zirconium nitride (ZrN) possesses a distinct oxidation resistance, where zirconium oxide (ZrO_2) formation on the surface has a similar effect of restraining oxygen diffusion to grains inside the film. Nevertheless, oxidation resistance in those films does not surpass 873 K [27,30]. Silicon addition to ZrN thin films is an interesting technical alternative to increase its oxidation resistance.

Although many reports in the literature demonstrate the advantages of silicon addition in MeN thin films [1,12–22,24,31], there are gaps and divergences regarding the formation mechanism of microstructure in Me-Si-N thin films, as well as the influence of Si content and deposition parameters over the physical and chemical properties of the coatings. That is due the constant development in the area, thus new ongoing studies try to explain the phenomena associated with obtaining coatings with enhanced properties against oxidation, corrosion and wear.

This work reports on the influence of silicon addition (0 to 15 at.%) of Zr-Si-N thin films. Those coatings were characterized by RBS, GAXRD, SEM, XPS, nanohardness and oxidation tests.

2. Material and methods

Zr-Si-N thin films were co-deposited by reactive magnetron sputtering with an AJA Orion 5-HV Sputtering Systems model using two individual targets, zirconium and silicon, with 99.97% and 99.99% purity, connected to a DC and RF power supply, respectively. A rotatory sample holder was located at 120 mm of distance between targets and substrate. A summary of main sputtering deposition parameters and material characteristics utilized in the experiments is listed in Table 1.

All deposition parameters were maintained constant during depositions except the power applied in silicon target, which was set at six values: 25W, 50W, 75W, 100W, 125W e 150 W.

Silicon wafer and polyethylene (PE) were employed as substrates. The films deposited on silicon wafer substrate were characterized by Grazing Angle X-ray Diffraction (GAXRD), non-monochromated X-ray Photoelectron Spectroscopy (XPS), nanohardness and oxidation tests, whereas the films deposited on PE were analyzed by Rutherford Backscattering Spectrometry (RBS).

Samples undergone ultrasonic bath in acetone for 30 min. Additionally, immediately before being placed in deposition chamber, Si substrates were cleaned with hydrofluoric acid to remove native SiO_2 layer.

Table 1
Main deposition parameters.

Power to Zr target	120 W
Power to Si target	25 to 100 W
Ar flow rate	19 sccm
N_2 flow rate	2 sccm
Base pressure	1×10^{-6} Pa
Work pressure	4×10^{-1} Pa

RBS at 2.0 MeV was performed with α particle on a 3 MV Tandetron equipment. The analysis was made by a silicon detector positioned at 165° of incident beam and 12 keV resolution in the tests.

Microstructure of the films were analyzed by GAXRD with Shimadzu LabX XRD-6000 instrument, using Cu K_α radiation (40 kV and 30 mA) of 0.154 nm wavelength at an incident angle of 5° and a step size of 0.02° and 2°/min scan speed. Measurement values were obtained at 2Θ from 24° to 60° and peaks were identified by comparison with International Centre for Diffraction Data (ICSD) data files. The XRD data was used to calculate crystallite size by Scherrer, preferential orientation with Harris method [32,33], volumetric fraction of silicon and surface coverage [18].

X-ray photoelectron spectra (XPS) were recorded using a hemispherical spectrometer PHOIBOS 150- SPECS, equipped with X-ray Gun (XR-50) with an Al Kα source (soft X-ray source at 1486.6 eV, which is non-monochromatic). The base pressure in the analysis chamber was about 10^{-8} Pa. The anode was operated at 10 W (10 kV, 10 mA) and the analyzer was operated at a constant pass energy of 50 eV for survey spectra and 20 eV for selected regions. Before analyzes, all samples were subjected to surface cleaning with Ar^+ (1.0 KeV) sputtering procedure for ten minutes. The ion source IQE12/38 from SPECS was used, which allows the operation at 5 KeV beam energy. The incidence angle is preselected to be 50°, as the sample was not tilted (rotation angle at 0°). The binding energy shifts due to surface charging were corrected using the C 1s level at 284.6 eV, as an internal standard. All spectra were performed twice and C 1 s position was measured at the beginning and at the end of each experiment. The spectra were Shirley background-subtracted across the energy region and fitted using CasaXPS Version 2.3.15.

Nanohardness and modulus of elasticity values of the coatings were measured using a IHT Fisherscope HV 100 equipped with a Berkovich diamond indenter. A dynamic load-unload cycle, with load graduated increase and decrease, was applied for 40 s in each sample. The following parameters were standardized in the analysis: use of a 40 nm maximum indentation depth load cycle; cycles run at intervals of 40 s loaded to minimize the effects of the experiment in terms of viscoelastic deformation of the samples; 40 s unloaded (from 40 nm to zero). The load curves were used to calculate the film hardness and the unload curve and the corresponding deflection were recorded and used to calculate the elastic modulus using Oliver and Pharr method. A detailed explanation about these calculations can be obtained elsewhere [34]. For each sample, seven points were measured and the average hardness and standard deviation were obtained.

Scanning Electron Microscope (SEM) analyses were realized on a JEOL JCM 5700. Oxidation tests were performed by muffle oven for 30 min at 773 K, 873 K, 973 K and 1073 K, with heat rate of 10 K/min. The test temperatures were selected so that it can estimate those where decomposition of nitrogen and oxidation reaction processes begin. After oxidation tests the films were analyzed by GAXRD to identify in which temperature the oxidation products peaks occur and SEM in order to observe the surface morphology. Similar procedure was reported previously by other researchers [35–37].

3. Results and discussion

Golden metallic color, characteristic for stoichiometric ZrN thin films [12,26,38,39], was achieved for deposited films. Zr-Si-N reflected different shades of grey, depending of silicon content.

3.1. RBS

All films deposited on polyethylene were analyzed by RBS aiming to determine chemical composition of the coatings and resulting graphs