

## Superhard nanostructured coatings: structure and properties relations

*L. Rebouta<sup>a</sup> (rebouta@fisica.uminho.pt), F. Vaz<sup>a</sup>, S. Carvalho<sup>a</sup>, K. Shein<sup>b</sup>*

<sup>a</sup>University of Minho, Physics Department, Azurém, 4800-058 Guimarães, Portugal

<sup>b</sup>Institute of Solid State Chemistry, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg GSP-145, Russia

### Abstract

Nanocomposite thin films consisting of both nano-size solid solutions and nano-size polycrystalline materials embedded in various amorphous matrix materials provide a great potential for mechanical devices. Special attention will be dedicated to Ti-Si-N and Ti-Si-Al-N films prepared under conditions out of thermodynamic equilibrium, and the formation of mixed phases. In order to explain the influence of Si → Ti substitution in the bulk stoichiometric B1 TiN, calculations using first principles density functional theory were performed. A 16-atomic supercell  $Ti_7SiN_8$ , which corresponds to the nominal composition of  $Ti_{0.875}Si_{0.125}N$  was used as a model. A lattice compression in result of Si-Ti substitution was obtained, which explains the experimental results.

These results suggest that, when surface mobility is reduced, the subsequent formation mechanism of nanocomposite of the type nc-MeN/a-Si<sub>3</sub>N<sub>4</sub>, results from the ion irradiation induced effects and a driven Si surface segregation, leading to continuous renucleation during film growth, which occurs in competition with the spinodal phase segregation.

This mechanism explains the grain size behaviour together with lattice parameter and the formation of a multiphase system, where the crystalline TiN, (Ti,Al)N and (Ti,Al,Si)N phases were identified by X-ray diffraction, when the surface mobility is not enough to obtain a complete thermodynamically driven segregation. XPS measurements show the absence of Titanium Silicide and the formation of the amorphous Silicon Nitride phase. These results show that a multiphase system of the type nc-TiN/nc-(Ti,Al)N/nc-(Ti,Al,Si)N/a-Si<sub>3</sub>N<sub>4</sub> can be formed. This multiphase system revealed a formation of thermally very stable superhard nanostructure, with a significant hardness increase with annealing at 800°C, which was retained up to 1000 °C.

Keywords: superhard coatings, nanocomposite, two-phase, Ti-Al-Si-N

Topic: Hard Coatings