
The crystal structure of TiN is known to be of the NaCl type, in correlation with the ratio between the atomic radii of its components. It is described as a close-packed isometric structure of titanium, in which nitrogen occupies all octahedral sites. This phase is stable for x values between 0.6 to 1.2, where over-stoichiometry is explained by vacancies in the titanium lattice.

In the present work the existence of a new structure of the CaF₂ type was revealed in the TiN system. This structure was observed in thin films obtained by reactive sputtering, using high levels of nitrogen in the plasma. It was found to be stable at room temperature, transforming into the normal NaCl structure, when heated. The characteristics for amorphous and crystalline films are presented in detail.