Abstract

During this research thesis, thin films of TiN_x, TiB_2 and multilayer composites of Ti/TiB_2 and TiN/CrN were fabricated employing the dc magnetron sputtering technique in an unbalanced configuration. The morphological characteristics and the structural properties of the films were studied with X-Rays techniques, while their electronic properties were examined through the use of Spectroscopic Ellipsometry (SE).

In-situ and real-time SE, has been used as a tool for the investigation of the co-relation and the underline physics between visual appearance and optical and electronic properties of TiN_x nanocrystalline coatings. As the N_2 content in the gas discharge guides the nitrogen composition in the film, appoints it the key parameter in color control for TiN_x sputtered films. The observed color variations can be resolved in terms of the Drude-Lorentz model; this describes the optical response of the conduction and valence electrons. The screened plasma energy (ω_{ps}) was used for the in-situ determination of stoichiometry according to refs. [4.7, 4.13, 4.14]. Color variations were identified through the Tauc-plot method which provides a wide band gap through the extrapolation of the linear part of $\omega \cdot [\varepsilon_2(\omega)]^{1/2}$ to zero coordinate. According to SE results variations in stoichiometry, away from the ideal $x = 1$, can be attributed to N vacancies in the case of $x < 1$, while N interstitials are playing an important role for $x > 1$. In addition, ab-initio calculations were performed to reveal the importance of point defects in TiN_x. Since departure from the nominal 1:1 stoichiometry is often observed, defects play an important role on TiN_x physical properties. It was found that the interaction between two vicinal N vacancies is slightly repulsive and that the migration of such a defect has activation energy of 3.8eV. This high value of diffusion barrier for a N vacancy underlies the thermal stability of TiN_x. On the contrary, overstoichiometry is appointed by N interstitials. The diffusion energy of N interstitial migration is lower enough to assume that TiN_x films, with $x>1$, are less stable.

The effect of ion bombardment in structural and electronic properties of TiB_2 thin films was extensively studied. Stoichiometry, x, of TiB_x film varied from 2.1 – 2.23 showing a strong correlation with the deposition parameters, i.e the substrate bias voltage $|V_b|$. The increase of $|V_b|$ favors the growth of crystallites over the [001] orientation. In addition, the unit cell size was found to increase with stoichiometry. This is caused from the presence of compressive stresses on the one hand and defects (B interstitials) on the other. Employing the in-situ and real-time SE we manage to get insights in the deposition mechanisms of TiB_2. Finally we report on the mechanical properties of the TiB_2 thin films. The hardening of the films can be attributed to three different mechanisms: densification, grain size and the presence of defects.

Especially the relation of the grain size with the hardness of the films reveals a reverse Hall-Petch effect.

The final part of this research thesis deals with the study of interface properties of Ti/TiB_2 multilayers and the microstructural characteristics of TiN/CrN multilayers. In the case of Ti/TiB_2 multilayers analysis was performed using low angle X-Ray techniques and SE. The study revealed the effect of the rotation speed and V_b in the morphological characteristics of the individual layers. The interface roughness was found to increase, increasing the rotation speed of the substrate holder and lowering the $|V_b|$ values. All the films exhibited very good periodicity. Only in the case of the multilayer films grown at -200V and 9rpm a dieviation from the long range order was observed. Results of X-Rays techniques are in good agreement with images of transmission electron microscopy. SE proved to be a valuable tool for the consideration of the individual layer thicknesses. Finally, the effect of the bilayer period on the microstructural characteristics of TiN/CrN multilayers was studied. In all cases [111] crystallographic orientation is favored. Increasing the rotation speed, of the substrate holder, results in higher strain of the unit cell and simultaneous growth of compressive stresses.