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Summary PhD Thesis "Multifunctional titanium nitride thin films"
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Summary

The aim of this thesis is the study of titanium nitride (TiN) thin films deposited by Direct Current (DC) reactive magnetron sputtering. The main objectives of this thesis are: the deposition of TiN epiaxially grown thin films on $Ni_{95}W_5$ with applications as buffer layer in superconducting architectures and TiN thin films deposited on carbon steel and Si (100) substrates with applications in tribology. To achieve these goals, a DC reactive magnetron sputtering equipment has been designed and built by means of the TiN thin films were successfully deposited.

The PhD thesis contains six major chapters with the corresponding references at the end of the thesis.

Chapter 1 is dedicated to the current research status on TiN coatings obtained by DC reactive magnetron sputtering.

Chapter 2 presents all the investigation techniques with applications used in the characterization of TiN thin films epitaxially grown on biaxially textured $Ni_{95}W_5$ substrates with applications as buffer layer in superconducting architectures and TiN thin films deposited on silicon and carbon steel substrates for tribologycal applications. For this purpose, the following techniques have been used: X-Ray Diffraction (XRD), Optical Microscopy, Atomic Force Microscopy (AFM), Scanning Electron Microscopy, X-ray Photoelectron Spectroscopy, nanoindentation and wear tests.

Chapter 3, ***Chapter 4*** *and* **Chapter 5** *comprise the original part of the doctoral thesis.*

Chapter 3 is dedicated to the design and assembling of the DC reactive magnetron sputtering equipment. The sputtering chamber has a diameter of 338 mm and a height of 451 mm and entirely made of austenitic stainless steel. The lower part of the chamber enclosure allows the installation of a turbomoleculare pump, two inclined magnetrons and an additional current fit through. To precisely adjust and control the inlet working gas, the deposition facility is equipped with two flowmeters, one for argon (neutral gas) and one fore nitrogen the reactive gas. In order to measure the pressure, the deposition facility is equipped with a measuring equipment using thermal and an ion gauge that are connected to the gauge controller. The two magnetrons are placed in an inclined position (24º between the symmetry axes), at a distance of 20 mm between the magnetrons. This way of positioning mode of the two magnetrons allows the deposition thin films by the simultaneous sputtering from two different targets, mounted on the two magnetrons.

It should be noted that mounting the magnetrons with parallel axes has the disadvantage of a low deposition rate when using two magnetrons simultaneously, the sample is placed laterally with respect to the axes of both magnetrons. It is well known that the deposition rate decreases with the increase of the distance between the target and the substrate, especially with the increasing distance from the simmetry axis of the magnetron. Both magnetrons are using 2 inches targets.

The substrate holder is made of austenitic stainless steel in which a resistive heating element has been mounted so that the samples may be heated up to 800ºC. In this context, the maximum heating temperature of the samples will not exceed 700ºC during the deposition temperature of TiN.

The lower body is designed to allow mounting a turbomolecular pump with a pumping speed of 500 l/s. This way it eliminates the possibility of oil vapor migration from the preliminary vacuum pump to the working chamber, a phenomenon common in systems equipped with mechanical pumps. Also, it ensures the achivement of a high pumping speed.
The lower body of the chamber allows installing multiple passes and current fit through.
Using this deposition system, the base pressure of 10^{-7} Torr (1.33×10^{-5} Pa) was reached in ~ 7h.

Chapter 4 is dedicated to $YBa_2Cu_3O_{7-\delta}$ high temperature superconducting materials for coated conductors. A coated conductor (CC) consists of a metallic substrate, which must develop a biaxial texture one or several oxide buffer layers and a superconducting layer of high quality, with intergrain misorientation smaller than ~ 4-6 º. The crystallographic texture can be achieved by different techniques applied to the substrate (Rolling Assisted Biaxial Texture, RABiT) or to the buffer layers (Ion Beam Assisted Deposition, IBAD). Finally, the deposition of the TiN buffer layer and the superconducting layers can be performed by vacuum deposition techniques (Laser ablation, evaporation etc.) or on non-vacuum chemical processes (Chemical Vapour Deposition (CVD), Chemical Solution Deposition (CSD)). The key issue is to prepare a textured substrate adequately buffered with TiN layers which transmits, totally or partially, the underneath structure to the superconducting layer.

Chapter 4 presents a detailed structural study on TiN epitaxial thin films deposited on $Ni_{95}W_5$ biaxially textured substrates by DC reactive magnetron sputtering. TiN is used as a buffer layer between the $Ni_{95}W_5$ and $YBa_2Cu_3O_{7-\delta}$ layers. Structural investigations were carried out using X-ray diffraction. Based on the X-rays diffraction analysis, it was concluded that the TiN film have epitaxially grown on the $Ni_{95}W_5$ substrate.

The High Resolution X-Ray Diffraction patterns recorded for the TiN films deposited in temperature range 400-700 ºC have indicated only the presence of a (200) reflection both for the substrate and the film. This indicates that the film grows with (h00) texture. Moreover, the φ scan type measurement recorded for the (311) substrate and film reflections have demonstrated that the film is epitaxially grown on the NiW substrate, with the following epitaxial relation: TiN[001](100)//NiW[001](100). Other phases and orientations were not observed in the limit of the measurement accuracy, except for the film deposited at 700ºC. For this, the (111) TiN polycrystallin peak at 36.51 degrees was identified.

The out-of-plane lattice parameter was calculated using the angular position of the (200) TiN peak. The obtained values are close to those corresponding for the bulk and exhibit a slight dependence on temperature. A slight increase in lattice parameter is observed to the samples deposited at substrate temperatures higher than 600^{o}C.

Further on, the dependence of the TiN grain sizes on the $Ni_{95}W_5$ substrate temperature during the growth is also presented. One can observe that at temperatures ranging between 400 and 500^{o}C, the crystallite sizes have a slight increase. Instead, from 500^{o}C to 600^{o}C a sharp increase to a much larger size can be observed, and then a sudden drop for the 700^{o}C deposited film. It is known that by increasing the deposition temperature, also increases the crystallite sizes. The deposition temperature of 600^{o}C is the limit between the epitaxial growth and the appearance of polycrystalline peaks. Thus, the decrease in grain size at 700^{o}C can be associated with the appearance of a TiN poly-phase.

In order to characterize the out-of-plane crystallites orientation distribution of the TiN films, Rocking Curve (RC) measurements around the (200) reflection were performed. The RC measurements were carried out for two different azimuths corresponding to the substrate rolling direction (RD) and the transversal direction (TD). We have chosen to perform measurements for these particular orientations because the substrates were cold rolled, and, as a consequence the crystallites are elongated on the RD. Therefore, the degree of orientation along the RD is much higher than along the TD. The films retain a similar behavior, although the overall degree of orientation is higher.

Using the X-Ray measurements we can conclude that the optimal temperature for depositing TiN on the $Ni_{95}W_5$ substrate is 500°C because this is the highest deposition temperature for which the grain size is still relative small, which will ensure a good surface morphology. Also, the epitaxial structure is preserved without any sign of other phases and orientations.

Following, we have studied the influence of the film thickness on the structural properties of the film deposited at the optimized temperature of 500°C. The XRD patterns indicate that the film retains the epitaxial characteristics for thicknesses up to 520 nm, with no sign of other phases and orientations.

The lattice constant shows no clear evolution with the film thickness and remains close to the bulk value. The lattice parameter values were calculated with error bars, showing that the experimental value is close to the theoretical one.

As far as the evolution of the Full Width at Half Maximum (FWHM) of the RC measurements with respect to the thickness of the deposited TiN film, it can be concluded that the films retain a similar behavior, although the overall orientation degree is higher.

Chapter 5 is dedicated to the study of TiN tribological layers that were deposited on carbon steel and Si (100) substrates. The surface morphology of the deposited layers was examined using AFM. Structural investigations were carried out using X-ray diffraction. Based on X-rays diffraction analysis it was concluded that the TiN layers have a crystalline structure with the grain size below 100 nm.

From the AFM measurements on samples S5 and S6 it is shown that the deposited films (by DC reactive magnetron sputtering, with an additional negative polarization of -90V), have a lower roughness value of the film surface as compared to the films deposited without a negative bias. The surface roughness of the TiN films is also influenced by the substrate temperature at which the deposition process takes place. The proof are the results of the AFM measurements (Root Mean Square roughness and Peak to Valley distance) on samples S3 and S4. The AFM measurements on these samples show that the influence of the polarization is much stronger than the influence of the substrate temperature.

From the X-Ray reflectometry analysis results that the thickness of the S1-S4 films is 163 nm, while the thickness of the S5, S6 films is 489 nm. From the analysis of these diffractograms some conclusions can be drawn about the influence of the deposition process parameters (substrate temperature, substrate polarization) on the orientation of the crystallites and the grain sizes.

Regarding the TiN films deposited on non-polarized substrates, the grain orientation is randomly distributed for the film deposited at 100 °C (sample S1) and a tendency for the development of the (200) texture is observed with the increase of the temperature up to 300 °C. By polarising the substrate at -90 V, due to the significant energy increase of the ions, a strong change in the orientation of the TiN crystallites is noticed. Thus, at a temperature of 100 °C the TiN layer shows a complete (111) texture, the other two diffraction peaks {(200) and (220)} being completely absent. At a temperature of 300 °C only the diffraction peaks corresponding to the crystallographic planes (111) and (220) appear on the diffractograms. Based on the results obtained by X-ray diffraction analysis one can conclude that the TiN layer texture varies from a random orientation of the crystallites to a strong texturing along a certain crystallographic direction, by the appropriate modification of the substrate temperature and ion bombardment conditions.

Thicker TiN layers were deposited on carbon steel in order to facilitate the microhardness measurements. The depositions were performed at a temperature of 300 °C. When deposited on steel substrates the films show a random orientation of the TiN crystallites in the absence of the substrate polarization and the disappearance of the (200) reflections when polarized of polarization. Consequently, the substrate nature has a minor influence on the TiN layers texturing at these low deposition temperatures. The grain size was determined based on the diffraction (111) line, present in all the films. The films deposited at 100 °C temperature have larger grain size than those deposited at 300 °C and the same decrease in the grain size is observed by negatively polarizing (-90V) the substrate during the deposition

Chapter 6 is dedicated to the general conclusions and the personal contribuitions brought to this thesis.

Keywords*: titanium nitride, sputtering deposition, epitaxial thin films, buffer layer, tribological coatings*

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