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EXECUTIVE SUMMARY OF THE THESIS

Metastable Ti FCC films produced by PLD: synthesis and characterization

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY – INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

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1. Introduction

Titanium, thanks to its high specific strength, thermal stability, excellent corrosion resistance in harsh conditions and intrinsic biocompatibility is a very attractive material for aerospace sector, process industry and biomedical application [1]. As the transition metals of the same group, it is an allotropic element that exhibits different phases according to the specific range of temperature and pressure. At room temperature and atmospheric pressure Ti shows the presence of a hexagonal-closed-packed HCP crystal structure (α phase), while at temperature above 882°C the crystal structure transforms into a body-centered cubic BCC one (β phase). According instead to the pressure induced transformation, Ti exhibits a hexagonal cell with three atoms per unit cell when the pressure is of 2-7 GPa, ω phase [2]. Recent studies also revealed the presence of a metastable face-centered cubic FCC phase, not predicted by the usual temperature-pressure phase diagram. Interestingly, the following has been characterized by different mechanical and electronic properties with respect the α phase. It has first been discovered upon depositing pure titanium onto a NaCl substrate by vacuum evaporation in epitaxial regime [3]. However, the FCC phase is found to be stable until a thickness of 20-30nm. Successively the same phase has been attempted to stabilized also by Direct Current Magnetron Sputtering (DCMS) and High-Power Impulse Magnetron Sputtering (HiPIMS) [2], but it has been reported to form only in the HiPIMS samples and until a thickness of 370nm. The different results among the different deposition techniques are related to the different energy regimes of the species deposited. The marked interest in this metastable phase leads to the study of the FCC phase also in bulk titanium, in which plastic deformation and impurities (H, O, N) seem to play a stabilizing effect [4]. The presence of impurities is coherent with the fact that titanium is a getter element and that the lattice parameters of FCC cells are found to be different among the different production techniques, varying from 4.09 Å to 4.33 Å [4]. In this context, this work aims at investigating the stability of FCC phase by Pulsed Laser Deposition

(PLD) at the varying of process conditions focusing on the role of thickness and oxygen content. The choice of PLD is related to its extreme versatility in exploring a wide range of energy regime (10s eV-100s eV) and to its capacity of establishing an out of equilibrium dynamics, thus stabilizing the metastable phases [5].

2. Materials and methods

2.1 Pulsed laser deposition

The deposition of titanium films on top of Si wafer (100) have been carried out thanks to the use of PLD. It is a PVD technique, in which an intense, nano-second pulsed laser is exploited, that passing through a focusing lens and a transparent window, vaporizes the target material promoting the formation of the relative plasma plume and its consequent condensation on the substrate. The different depositions have been made in vacuum and in controlled atmosphere of Ar (1Pa) at different values of initial background pressure[1], deposition time and fluence rate. The laser adopted consists of the second harmonic of a Nd: YAG source, with wavelength $\lambda = 532$ nm, repetition rate f = 10 Hz and pulse duration around 6 ns. The target used is titanium with a purity of 99,995 and a distance from the substrate of 7 cm. The substrate has no misalignment, and it undergoes rotation with a fixed value of 11 rpm. The target has been subjected to vertical translation of ± 20mm with a constant rotation of 495°/s. The vertical motion is controlled thanks to an opportune software that permits to control the velocity profile during the deposition. It is important to point out that after each deposition the window needs to be cleaned to avoid undesirable loss in the fluence rate. All the films have grown at room temperature with different deposition times, with fluence rate values of 2-10 J/cm^2 and initial background pressure of 10^{-4}-10^{-2} Pa. Some of the samples have undergone a post-deposition annealing at 400°C and 550°C for 1 h in a high vacuum chamber. The vacuum pressure during annealing experiment is of $5*10^{-5}$-$7*10^{-5}$ Pa. The heating ramp is fixed to 10°C/min.

2.2 Characterization techniques

Morphology and chemical analysis have been performed both in cross and plane view. In this work a Field Emission Zeiss SEM SUPRA 40 based on a GEMINI column is employed. The parameters adopted for the morphology analysis are the working distance of ≅ 4mm, an accelerating voltage of 5-6kV and an aperture of 30μm. For compositional analysis AZtec EDXS software was employed, where the aperture is fixed to 120 μm and the working distance to ≅ 8 mm.

XRD analysis has been made to assess the phase stability and the relative properties (cell dimensions, grains dimensions and microstrain) at different working conditions.
XRD diffraction measurements have been carried out both in Bragg/Brentano and grazing incidence configuration. The second configuration has been adopted to avoid the background signal of the substrate and to detect all the crystallographic planes irrespective of the favored orientations. In both the measurements an X-ray radiation from a CuKα source has been exploited.

Raman analysis has been performed to evaluate eventual Ti-O vibrational modes. In this work a Renishaw InVia micro-Raman spectrometer is adopted, equipped with optical microscope. The laser is an argon ion source that emits in the green (514nm).

3. Titanium getter function and compositional analysis

Before discussing the properties of titanium films, it is important to highlight the evidence of getter function of titanium and its effect on the variation of initial background pressure. The strong affinity of Ti to interact with impurities finds evidence during the ablation of the target, in which a strong decrease of chamber pressure is observed. The following mechanism is compared with the pumping curve of turbomolecular pump alone. As observed in Figure 1, for pressure ranges lower than $1*10^{-3}$ Pa the ablation of titanium is always

[1] With initial background pressure is intended the vacuum level of pressure reached before to start deposition.

more effective than turbo pump; furthermore, it is evident that increasing the fluence rate increases the amount of titanium in the chamber and the relative pumping rate. However, compared to the pumping curve of turbo, the following shows a non-monotonic trend with some oscillations around 10^{-5} Pa, symptom of a different dynamics of pumping. The important conclusion from this behavior of titanium is that the initial background pressure is not a constant process parameter, but it changes during the deposition time.

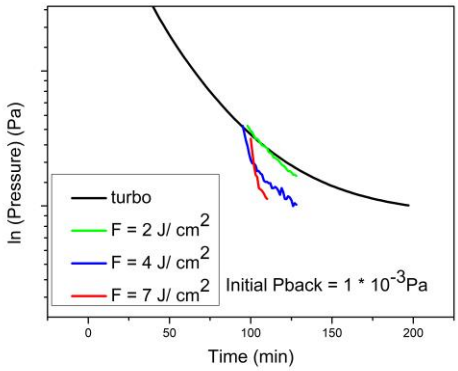

Figure 1: Comparison of turbomolecular pumping curve with that related to the ablation of titanium for different fluence values.

The following aspect is coherent with the compositional analysis performed by EDXS, in which emerges an atomic concentration of oxygen higher than 30% in all the samples. Titanium films are characterized by the only presence of Ti and O. Since the last one seems to play a significant role in the stabilization of FCC phase [4], here it has been analyzed its atomic concentration with respect to the different process parameters. From the EDXS analysis of all the samples, it has been noted that the amount of oxygen in the films does not depend on the initial background pressure and on the fluence rate, but only on the deposition time. From Figure 2 it is evident that the quantity of oxygen increases with high speed for smaller deposition times, while for higher ones it tends to stabilize to an equilibrium value of around 40%. It means that, irrespective of the deposition time, the film will be always metallic and will never achieve the threshold quantity to form an oxide.

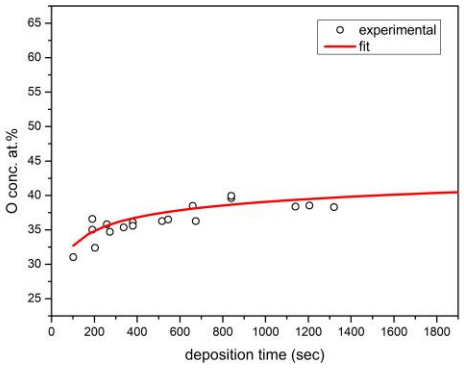

Figure 2: Atomic oxygen concentration in titanium films as a function of deposition time. The red fitting curve has a logarithmic trend.

4. Morphological analysis

The morphology of titanium films (Figure 3) is characterized by a columnar growth, in accordance with the high energetic regime of PLD that in vacuum promotes the formation of compact and oriented films. Almost all the samples with a thickness of 50-600 nm share the same morphology of Figure 3, irrespective of the working conditions (fluence, deposition time, background pressure). The only difference that may be spotted arises for the high thickness samples. In this case the morphology display a less defined columnar and a more random growth, maybe related to the higher residual stresses present in the film (Figure 4).

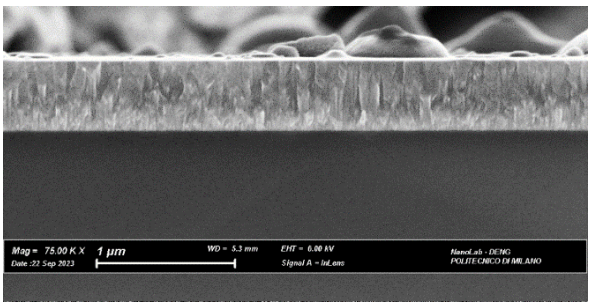

Figure 3: Cross-sectional SEM image showing the typical compact columnar morphology of Ti films by PLD with a thickness of 50-600nm.

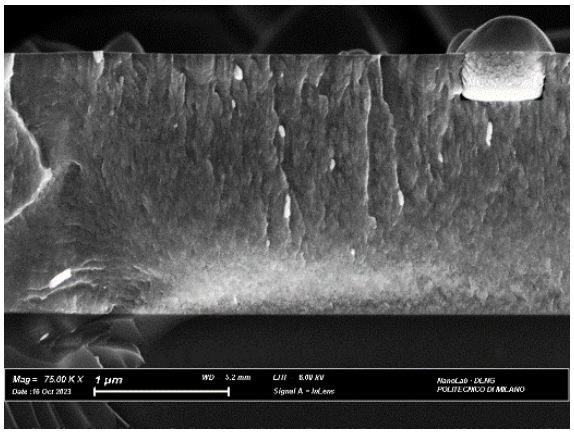

Figure 4: Cross-sectional SEM image showing the morphology of Ti films by PLD with a thickness of 2µm.

5. Investigation on crystal phase stability

The main part of the following work regards the XRD analysis, both in grazing and in Bragg/Brentano configuration, to investigate the stabilization of the FCC phase at different thickness, oxygen concentration and in atmosphere of 1 Pa of Ar.

Firstly, to understand which is the predominant phase of the films, the experimental diffraction patterns of samples have been compared with the reference powder diffraction patterns of HCP and FCC. The deposition conditions and the insufficient oxygen content in the film to form oxide permit to exclude the possible presence of BCC, ω and titanium oxides phases. While the presence of HCP Ti is suggested by the range of temperature and pressure during the depositions, the FCC presence is predictable due to the out of equilibrium regime imposed by PLD, that favors the formation of metastable phases. Figure 5 (next page) clearly shows the presence of a predominant FCC phase with a residue of HCP too. The former peaks position does not match the reference powder diffraction of FCC titanium (solid green lines) that are shifted toward higher angles with respect to our samples. This mismatch may be justified by the high amount of oxygen present in the film. This has been verified by applying Bragg law to each peak, leading to a convergent value of lattice parameter of 4.22-4.30 Å. For this reason, in Figure 5 it has been represented with the dashed lines the shift of reference powder diffraction of FCC due to oxygen contribution. On the other hand, the HCP peaks are not all evident and they almost match the reference positions (oxygen atoms are not expected inside this phase).

If in literature [2], [3] the FCC phase has turned to be stable only for limited thickness, in this work the metastable structure results to be always evident (until a thickness of 1922nm). It means that PLD has stronger tendency to form metastable phases compared to other mentioned deposition techniques. Despite this, it is important to note still some variations in the relative intensity of HCP phase, that becomes always more predominant at higher thickness. This confirms the fact that titanium FCC phase is still sensible to the thickness variation, also in PLD.

The deposition in gas atmosphere (1 Pa Ar) attempted at slowing down the strong energy regime of PLD, trying to transform it in a closer to equilibrium technique. In Figure 6 (next page) the effect of the gas atmosphere revealed to be influencing only at small fluences, favoring the quasi-total formation of HCP phase. This is coherent with the stabilization of metastable phases by PLD.

Regarding the effect of oxygen, it has been found by Tshwane that FCC phase is stable only in the range of Ti/O ratio between 0.77 and 1.66 [4] . For this reason, the variation of FCC peaks intensity at different Ti/O ratio has been evaluated. In this work it results that samples with Ti/O ratio higher than 1.66 do not exhibit FCC phase, confirming the theoretical calculus proposed by Tshwane [4]. Additionally, from Figure 7, it is observable that in

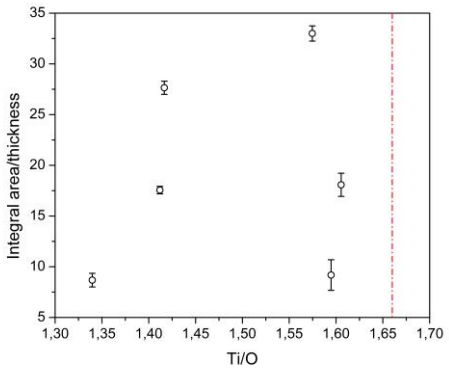

Figure 7: Intensity of FCC peaks with respect to Ti/O ratio. In red the upper limit proposed by Tshwane as indicated [4].

the range between 1.33 and 1.66, where FCC should be stable, the samples display a non-monotonic trend of the intensity of FCC peaks with respect to the Ti/O ratio. This trend may suggest that as we approach the upper and lower limits the FCC peaks are less intense.

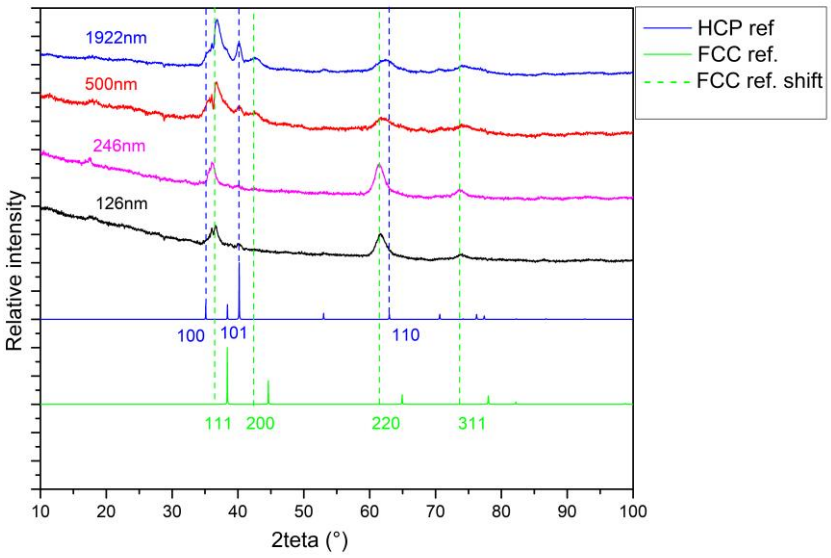

Figure 5: GIXRD patterns of titanium films as a function of thickness highlighting the relative variation of FCC and HCP peaks.

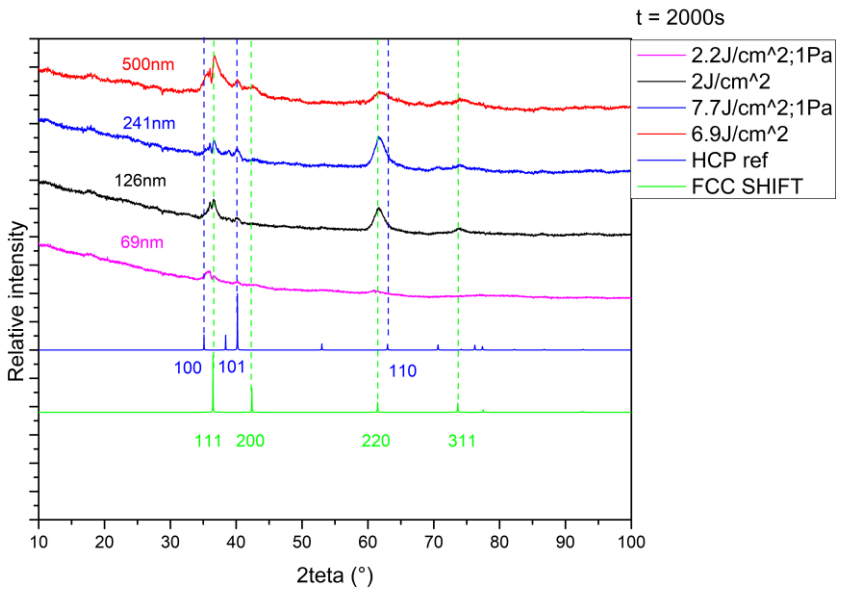

Figure 6: GIXRD patterns of titanium films highlighting the effect of Ar atmosphere at different fluences.

Thus, in the assumption that the quantity of oxygen inside HCP cell is negligible due to the non-shift of the peaks, it has been revealed that the number of oxygen atoms in the cell that stabilize the FCC phase should be around 3.

The last part of XRD analysis has been devoted to the analysis of Bragg/Brentano spectra and to the calculus of lattice cell properties (size, grains dimensions). Regarding the analysis of Bragg/Brentano spectra, the samples show up one and only single peak at 36° referred to (111) plane of FCC phase. It means that HCP crystallites are present, but they are not in favorable orientation. The analysis leads to coherent values in both the configurations, with a lattice parameter of 4.22-4.30 Å and grains dimensions of 13-21 nm. The variation of these parameters has been analyzed at different deposition conditions and revealed that all the samples present almost both the same cell and grains dimensions irrespectively of the deposition time, fluence rate and background pressure.

The very last part of this thesis has been devoted to the analysis of Raman spectra in which emerges, with increasing intensity as the Ti/O ratio reduces the presence of a broad band below 400cm^{-1}. This seems to be related to the high amount of oxygen in the films that may form some amorphous oxides.

6. Conclusion

In conclusion, the main objectives of the thesis have been achieved and some interesting research insights arised. The first important result is the stabilization of FCC phase at any thickness below 2 μm irrespective of the fluence rate, initial background pressure and deposition time, highlighting the important role of PLD. Nevertheless, within the scope of the work, appropriate strategies have been identified to facilitate the suppression of the metastable phase. Regarding this, it has been observed that the gas atmosphere (1 Pa Ar) at low fluence promotes the thermodynamically favored phase (HCP), and that the concentration of oxygen plays a fundamental role in stabilizing FCC phase. In fact, only for samples with 1.33 <Ti/O<1.66 FCC phase shows up. Furthermore, the lattice parameter of the following phase is almost coherent with the different values proposed in literature [4]. Although these goals have been achieved, there are still remaining open questions that require further investigation.

7. References

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