Tailoring the structural and surface properties of TiO_2 thin films and TiO_2-based nanolayers, with heat treatments, layer thickness, and oxide mixtures

Abstract

Titanium dioxide (TiO_2), also known as titanium (IV) oxide or titania, is naturally available on the Earth as a bright, fine, and white pigment. Thanks to its unique properties, such as high refractive index, chemical stability, photocatalytic activity, and self-cleaning surface, TiO_2 represents one of the most intensively studied compounds. The properties of TiO_2, which depend on its three crystalline phases (anatase, brookite, and rutile), have made this material a valuable candidate for applications in many fields, such as optics (Bragg reflectors, meta-surfaces, optical filters), electronic (sensors, phase-change memory and metal insulator-semiconductor devices), and photocatalysis (air purification, water treatments, self-cleaning coatings, dye-sensitized solar cells). Indeed, its band structure, long-term stability, non-toxicity, cost-effectiveness, and strong oxidizing power make TiO_2 highly suitable for wide environmental and energy applications. Moreover, given its impressive optical properties, TiO_2 finds room in the context of amorphous coatings for the development of dielectric mirrors, characterized by low transmittance and thermal noise, to be implemented in the detectors of gravitational waves. Given the impact that both structural and morphological properties have on the optical and electronic performances of TiO_2, a systematic study on the tailoring of TiO_2 crystal structure and surface properties is of fundamental relevance in many fields.

One of the aims of this work is thus to study the morphological, structural, and photocatalytic properties of amorphous TiO_2 thin films and the impact on these properties of the structural transitions induced by thermal annealing in different environments. Moreover, the tailoring of the morphological and structural properties of TiO_2 as a function of thickness is also investigated. Additionally, the combination of TiO_2, in its nanolayered form as well as in the state of co-sputtered mixture, with other metal oxides is analyzed to address the extent of their structural and morphological reliability for highly performant high-refractive index candidates in new generation Bragg-like reflectors. In this scenario, Scanning Probe Microscopy based experiments (Atomic Force Microscopy, and Kelvin Probe Force Microscopy), Raman Spectroscopy, and X-Ray Diffractometry have been used to study the morphological, photocatalytic and structural properties of the investigated materials.

An overview of the properties of TiO_2 and its applications, including the one for gravitational wave detectors, i.e., the context where this work arose, is given in Chapter 1. Here the main properties of some other metal oxides (i.e., ZrO_2, Al_2O_3, Ta_2O_5, Al_2O_3) encountered in this thesis are additionally discussed.

Then, Chapter 2 will briefly introduce the fabrication (ion-assisted deposition and ion-beam sputtering) and characterization (Raman Spectroscopy, X-Ray Diffractometry, Scanning Probe and Electron Microscopy) techniques used in this work.

The experimental results will be presented in Chapters 3,4,5, and 6. In particular, in Chapter 3 the effect of thermal treatments in different environments (air, oxygen and vacuum) and at different temperatures on the structural, morphological, and photocatalytic properties of TiO_2 thin films will be discussed. The influence of the annealing environment on the crystallization onset and evolution of both anatase and rutile phases, as well as on the thin film morphology and photocatalytic properties will be investigated.

Chapter 4 will be focused on the tailoring of the TiO_2 thin film crystallization temperature, in the anatase crystalline phase, by modulating its thickness from hundreds to few nm. Decreasing the layer thickness, an exponential increase of the crystallization onset temperature will be demonstrated. Moreover, the evolution of the crystallization will be studied in an annealing temperature range up to 1000 °C and correlated to the evolution of the phonon lifetime, studied by Raman spectroscopy.

The role of interfacing TiO_2 nanolayers with other nanolayered oxides (SiO_2, Ta_2O_5, Al_2O_3, or ZrO_2), in a similar Bragg-like reflector geometry at the nm scale, on the overall structural and morphological properties of the specimen will be discussed in Chapter 5. The presence of segmentation, as well as of the interfaces with other oxides, will be shown to significantly affect the crystallization onset temperature.

Then, the effect on structural and morphological properties of combining TiO_2, at different concentrations, with Ta_2O_5 in a co-sputtered mixture will be presented in Chapter 6. The influence of different substrates will be also showed.

Finally, results and conclusions are summarized.

In addition, Appendices are included to i) give an overview on the phonon confinement phenomenon, ii) illustrate theoretical nanolayers modeling and recent technical advances of the apparatus used for the sample fabrication within the Unisa/Unisannio collaboration, iii) describe the results and the knowledge acquired during my periods at the Lancaster University (UK) and at the Gestione Silo company (Florence, Italy).