CHAPTER 1

INTRODUCTION

1.1 Background

Today's microelectronics relies heavily on semiconductor-based technology which primarily exploits the charge of the carriers in the semiconductors. Aiming to achieve a new type of information technology with improved performance, lower energy consumption, and/or entirely new functionalities, the recent field of spin-based electronics or spintronics seeks to incorporate the spin degree of freedom into the conventional charge-based electronics.

The initial development of spintronics relies on the success of passive magnetoresistive devices, especially giant magnetoresistive and tunneling magnetoresistive devices, whose main components are ferromagnetic metallic multilayers.[1] Active spin-based semiconductor devices are the next stage in the development of spintronics technology. The paradigm of semiconductor spintronics is arguably the spin-field effect transistor (spin-FET) proposed by Datta and Das.[2] The theoretical basis of the spin-FET explores the possibility of controlling the spin of the injected carriers as they travel through a low-dimensional channel, connecting two ferromagnetic reservoirs (source and drain) by the electric field imposed by the voltage applied to the gate electrode. In order to achieve a practical device, the electrons must first be spin-polarized and then largely preserve their polarization as they travel through the semiconductor material. However, this will be hardly achieved using conventional ferromagnetic materials as reservoirs because of the conduction mismatch and spin scattering at the hetero-interfaces. Therefore, the design of materials combining both semiconducting and ferromagnetic properties turns out to be of crucial importance in the development of such devices.[3,4]

In this context, oxide-based diluted magnetic semiconductor (DMS) materials have been a subject of increasing interest due to reports of room temperature (RT) ferromagnetism in several systems and their potential easier integration with conventional nonmagnetic semiconductors for spin injection (*e.g.* Si, AsGa). Among the oxide-based DMS studied, Co-doped TiO_2 has attracted particular interest due to its ferromagnetic behaviour well above RT for low Co doping concentrations ($T_c > 650$ K).[5]

1.2 Scope

The main purpose of this thesis is to present a comprehensive experimental study on how the properties of pulsed laser deposited Co-doped TiO_2 thin films are affected by specific experimental parameters used for film growth. The parameters of interest in this work are the laser energy density, the substrate temperature and the composition and pressure of the background gas phase. The study provides new knowledge about the importance of these parameters in laser deposition of Co-doped TiO_2 thin films on sapphire at a wavelength of 248 nm. The work was carried out under the limiting condition that relatively low substrate temperatures (≤ 350 ºC) should be utilised.

1.3 Outline of the thesis

This thesis consists of six chapters, four of which comprise the main body of the thesis: an introduction to diluted magnetic semiconductors (Chapter 2), an introduction to pulsed laser deposition (Chapter 3), a presentation of the experimental set-up and characterization methods used in the preparation and analysis of the thin films (Chapter 4), and the presentation and discussion of the main experimental results (Chapter 5). The content of each individual chapter is as follows:

- Chapter 1 gives the background for work and an outline of the thesis;
- Chapter 2 offers an introduction to DMS materials and a review of the experimental status of the oxide diluted magnetic semiconductors (O-DMS), including recent results on the TiO_2-based system;
- Chapter 3 provides an introduction to pulsed laser deposition of oxides. A chronological review of its development is followed by a short list of advantages and disadvantages of pulsed laser deposition. Finally, the deposition process is described in three steps covering the target, the plume, and the film deposition;
- Chapter 4 describes the experimental set-up designed for this work and also gives a description of film characterisation methods. In general, the deposited films were

characterised by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FEG-SEM), Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), and Rutherford Backscatering Spectrometry (RBS). Optical transmission in the UV/VIS/near-IR, resistivity and magnetisation measurements were also performed;

- Chapter 5 presents the main experimental results with respect to the deposition of Co-doped TiO_2 as well as a discussion of these results. In this chapter it is demonstrated how Co-doped TiO_2 films phase composition, crystallinity and physical properties are strongly related to the deposition parameters of the PLD process. The optical properties of the Co-doped TiO_2 films as a function of the process parameters are examined in detail. The parameters changed in the PLD process were the laser energy density, total pressure, substrate temperature, background gas composition, and the flow rate of the different gases. Argon and hydrogen were chosen as background atmospheres.

  The influence of every process parameter are studied in detail in dedicated sections. The first section, "Co-doped TiO_2 thin films prepared at different laser energy densities (I)", presents experimental results that demonstrate how the crystallographic structure and optical properties of the films are influenced by laser energy density in the ablation process. Section two, "Co-doped TiO_2 thin films prepared at various total pressures (II)", contains a discussion of the influence of total pressure on the growth mode and properties of the films, mainly the percent of anatase and rutile phases in the PLD films. Section three, "Deposition of Co-doped TiO_2 films at different substrate temperatures (III)", describes the influence of variation of substrate temperature and substrate-to-target distance on the PLD thin films. The variation of these two parameters gives the unique opportunity to prepare films with crystallographic features that vary from amorphous to epitaxial without changing the pressure of the background gas or the substrate. Section four, "Deposition of Co-doped TiO_2 films at different Ar fluxes (IV)", describes the effect of introduction of an inert gas (argon) at different flow rates and its influence upon structural and optical properties of the Co-doped TiO_2 films. Section five, "Deposition of Co-doped TiO_2 films at different H_2 fluxes (V)" presents a study of how the addition of hydrogen during the ablation process affects the growth mode and properties – mainly optic and magnetic – of the thin films;

- Chapter 6 summarizes the results and discussions of Chapter 5, giving the main conclusions that might be drawn from our work, including suggestions for further studies.

1.4 References

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