Optimization of growth parameters of TiO2 thin films using a slow positron beam

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Abstract. TiO_2 thin films grown on fused silica were investigated using positron Doppler broadening spectroscopy at the slow-positron-beam SPONSOR [1] at the Helmholtz-Zentrum Dresden-Rossendorf. Effects of changes in different parameters like temperature or oxygen flow during film deposition on positron sensitive parameters have been investigated and first results will be presented.

1. Introduction

The ferromagnetic properties of transition metal doped TiO_2 are intensely investigated in recent years. Such dilute magnetic semiconductors (DMS) have potential applications in spintronics, i.e. due to spin-polarization of mobile charge carriers, or in magneto-optics. Ferromagnetic transition metal doped TiO_2 films can be created in different ways, i.e. from thin film growth or ion implantation. Until now there is an intense debate about the origin of the ferromagnetic properties and whether they are related to highly mobile spin-polarized electron currents or not. Consequently, highly sensitive structural investigations are applied which revealed that ferromagnetic properties may arise from either secondary phases [1], Co enriched anatase clusters [2] or intrinsic defects [3, 4]. Moreover, structural point defects such as vacancies can influence the ferromagnetic interaction between the transition metal dopants [5]. It was also found that Co doped TiO_2 can be ferromagnetic and insulating at the same time which can not be explained by the usual ferromagnetic double exchange model describing the coupling in DMS [6]. The major problem, however, is the occurrence of metallic Co secondary phases, especially in ion-implanted TiO_2 [7], which have the potential to mimic all of these effects and thus camouflage an intrinsic ferromagnetic coupling.

In future we will study the origin of ferromagnetic properties of V, Co or Mn doped anatase TiO_2 thin films. The effects of oxygen pressure and substrate temperature on the (defect) structure of the grown films are of importance concerning the film quality (for further treatments and investigations) and can be easily investigated by depth-resolving positron Doppler broadening spectroscopy.

Journal of Physics: Conference Series **443** (2013) 012073 doi:10.1088/1742-6596/443/1/012073

2. The SPONSOR setup

The Slow Positron System of Rossendorf (SPONSOR) [8] was used for depth-resolving Doppler broadening measurements. There positrons were implanted with energies between 27 eV… 36 keV resulting in an implantation depth of several micrometers (the planned film thickness is about 300 nm). The energy resolution at the annihilation line is (1.09 ± 0.01) keV.

3. Choice of the substrate material

The substrate material can have a strong influence on the film structure: TiO_2 films are either polycrystalline, if deposited on fused silica (a), or epitaxial, if deposited on $SrTiO_3$(100) (b). From (a) it is evident that the TiO_2 structure can be adjusted to be either rutile or anatase depending on growth temperature. The largest electric conductivities have been achieved for TiO_2 anatase films either undoped or doped with Nb. Besides $SrTiO_3$, $LaAlO_3$ may also serve as a possible substrate material. Depth-profiles obtained by Doppler broadening spectroscopy at SPONSOR for as-received material (figure 1) indicate that $SrTiO_3$ is the better candidate: the diffusion length L_+ (obtained by the VEPFIT package [9]) is more than double the value of that for $LaAlO_3$.

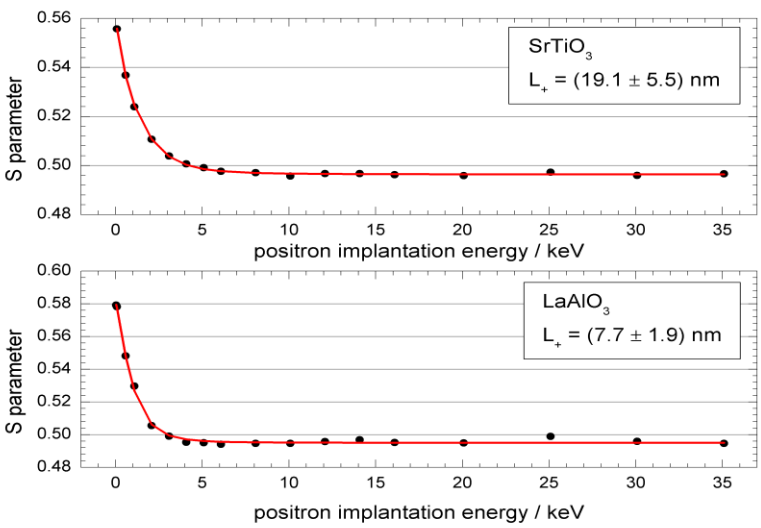

Figure 1. Depth profiles of substrate candidates for TiO_2 films. The diffusion length L_+ was calculated using the VEPFIT package [9].

Due to these investigations TiO_2 will be grown on $SrTiO_3$ for further investigations of ferromagnetic properties.

4. Effect of substrate temperature during film growth on the structure of TiO_2

Thin films of TiO_2 were grown by sputter deposition. The substrate temperature influences structure and defect situation of deposited films and influences defect induced room-temperature ferromagnetism. To investigate a temperature effect we used a series of thin TiO_2 films grown on fused silica where the films were deposited at constant partial oxygen pressure. The related profiles are shown in figure 2 also containing the profile of the substrate of fused silica (f-SiO_2). One can see the effect of the substrate on the S parameter but the layer is not affected by this meaning that the films are not too thin. Again the diffusion length L_+ and the S parameter of theTiO_2 film layer were calculated (figure 3). Surprisingly there is a non-monotonous behaviour of the S parameters with a maximum for a substrate temperature of around 400 °C. The small layer thickness leads to larger error bars for L_+ complicating the interpretation of results.

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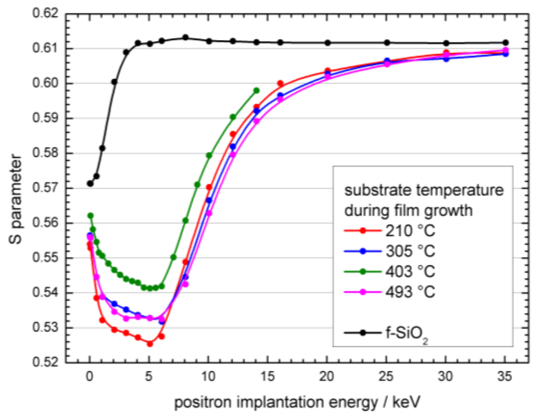

Figure 2. Depth profiles obtained by positron Doppler broadening spectroscopy for different substrate temperatures.

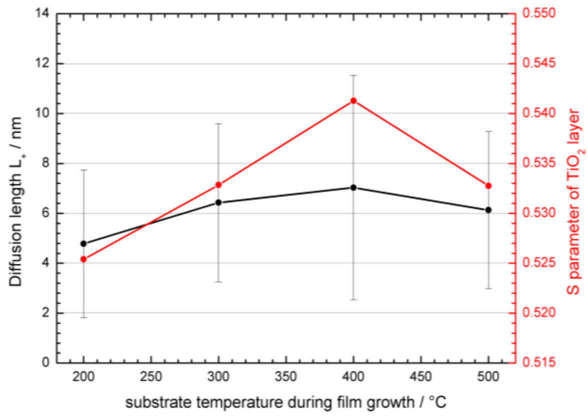

Figure 3. S parameter and calculated diffusion length L_+ (using the VEPFIT package [9]) for the TiO_2 films grown on fused silica (f-SiO2).

TiO_2 will be grown at 400 °C due to the optimum of the diffusion length for this temperature.

5. Influence of oxygen partial pressure during film growth on the structure of TiO_2

The origin of the ferromagnetic properties was explained by molecular orbitals formed from the valence electrons on the three Ti ions surrounding the oxygen vacancy and couple via direct exchange interaction. A direct relationship between the oxygen partial pressure during growth, the electronic conductivity as well as the saturation magnetic moment of anatase TiO2 films was established [3].

We used positron Doppler broadening spectroscopy to investigate the influence of oxygen partial pressure on film structure on a nano-scale. This investigated series consists also of TiO_2 grown on fused silica at a temperature of 400 °C at different oxygen partial pressures. The profiles (figure 4) as well as the extracted S parameters and diffusion lengths L_+ (figure 5) show a clear dependence on oxygen partial pressure. A simultaneous increase of S and L_+ indicates that with increasing pressure smaller defects begin to agglomerate, leading to larger values for S and L_+. The jump in L_+ (within the error bars) indicates a sensitive pressure range of around $4 \cdot 10^{-4}$ mbar.

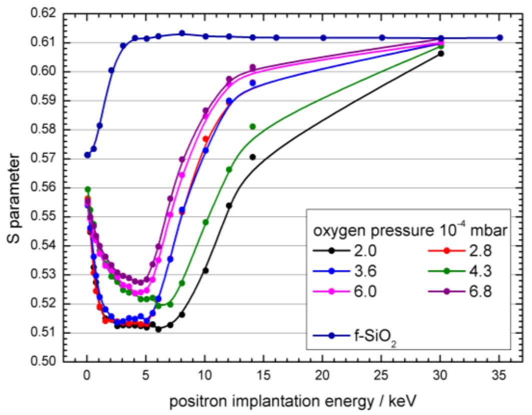

Figure 4. Depth profiles obtained by positron Doppler broadening spectroscopy for different oxygen partial pressures.

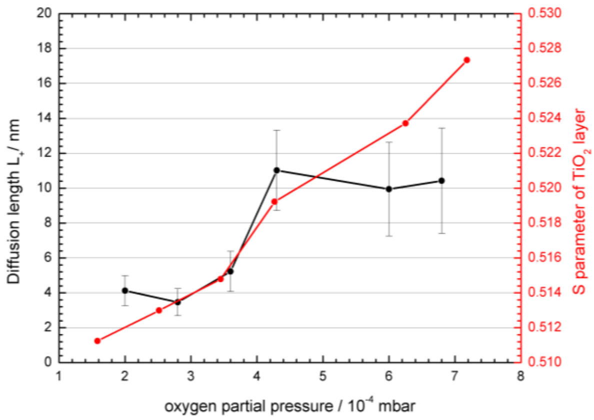

Figure 5. S parameter and calculated diffusion length L_+ (using VEPFIT [9]) for TiO_2 films grown on fused silica (f-SiO2) for different oxygen partial pressures.

6. Conclusions and Outlook

First pre-investigations for the investigation of thin TiO_2 films deposited on fused silica were done by using positron Doppler broadening spectroscopy. The aim was to improve the conditions during the film growth and to decide for a suitable substrate material within the framework of investigating the ferromagnetic properties of V, Co or Mn doped anatase TiO_2 thin films. $SrTiO_3$ was chosen as substrate material for the future film deposition. It also turned out that variations in substrate temperature and oxygen partial pressure have great influence on the defect structure of the films. Optimal parameters were found as following:

a) the substrate temperature should be in the range of 400 °C
b) at an oxygen partial pressure of around $4\cdot10^{-4}$ mbar present defects in the layer start to agglomerate

Next step will be the film deposition on $SrTiO_3$ at different substrate temperatures and oxygen partial pressures to investigate the effects also for this substrate material.

This work is supported by the Initiative and Networking Fund of the German Helmholtz Association, Helmholtz-Russia Joint Research Group HRJRG-314, and the Russian Foundation for Basic Research, RFBR #12-02-91321-SIG_a.

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