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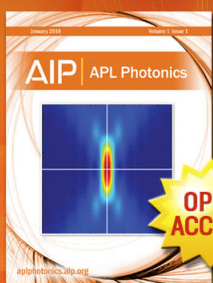
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The local environment of cobalt in amorphous, polycrystalline and epitaxial anatase TiO₂:Co films produced by cobalt ion implantation

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Amorphous, polycrystalline anatase and epitaxial anatase TiO₂ films have been implanted with 5 at. % Co⁺. The magnetic and structural properties of different microstructures of TiO₂:Co, along with the local coordination of the implanted Co atoms within the host lattice are investigated. In amorphous TiO₂:Co film, Co atoms are in the (II) oxidation state with a complex coordination and exhibit a paramagnetic response. However, for the TiO₂:Co epitaxial and polycrystalline anatase films, Co atoms have a distorted octahedral (II) oxygen coordination assigned to a substitutional environment with traces of metallic Co clusters, which gives a rise to a superparamagnetic behavior. Despite the incorporation of the implanted atoms into the host lattice, high temperature ferromagnetism is absent in the films. On the other hand, it is found that the concentration and size of the implantation-induced nanoclusters and the magnetic properties of TiO₂:Co films have a strong dependency on the initial microstructure of TiO₂. Consequently, metallic nanocluster formation within ion implantation prepared transition metal doped TiO₂ can be suppressed by tuning the film microstructure. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919702>]

I. INTRODUCTION

The discovery of above room temperature ferromagnetism (FM) in Co-doped TiO₂ (Ref. 1) has spurred intensive research on transition metal (TM) doped TiO₂. There have been huge efforts to find the optimal method to prepare, to understand^{2–6} and finally to apply⁷ such materials as dilute magnetic semiconductors (DMS). Although Co-doped TiO₂, in particular, Co⁺-implanted rutile or anatase TiO₂ (Refs. 8 and 9), shows promising magnetic properties for applications, the origin of the observed FM is still under debate. Most of the theoretical frameworks, which try to explain the possible mechanism of the long-range ferromagnetic order, consider the dopant-defect-host relation in terms of the local atomic coordination.^{10,11} On the other hand, further experimental studies showed that the magnetic TM dopant is not an essential ingredient in order to introduce FM in oxides. As already reported, oxygen-poor growth conditions¹² or grain boundaries¹³ can induce FM without the presence of any TM dopant. Moreover, the presence of a magnetic impurity dopant can lead to defect-induced FM in ZnO:Co system, in which dopant Co atoms remain paramagnetic.^{14,15} In addition, the TM-doping process, especially ion implantation, can often lead to metallic nanoclusters, giving rise to FM.¹⁶ To date, there has been reports to suppress ion implantation induced cluster formation by changing implantation conditions or by performing heat treatment.¹⁷ Consequently, identifying the local environment around TM dopants including their oxidation states along with possible aggregates is of primary importance to explain and to tailor magnetic and other physical properties of such systems. The purpose of this study is to determine the

effect of the initial microstructure on the dopant-host coordination along with the secondary phase formation, as well as the magnetic properties of Co⁺-implanted TiO₂ thin films.

II. EXPERIMENTAL

TiO₂ films of 300 nm thickness were grown on SrTiO₃ (100) single crystals by DC magnetron sputtering of a high purity oxygen deficient ceramic TiO_{2-x} target in Ar/O₂ atmosphere with ~0.4 vol. % of O₂. In order to prepare different structures of TiO₂, different substrate temperatures and post-growth annealing were applied. While amorphous films were obtained on unheated substrates, polycrystalline anatase was obtained by post-growth vacuum annealing of initially amorphous layers at 450 °C for 1 h at a pressure below 5 × 10^{−7} mbar. Epitaxial growth of TiO₂ anatase was achieved by keeping the substrate at 500 °C during deposition. Implantation of Co⁺ was performed using a 200 kV Danfysik implanter under an incidence angle of 10° to avoid channeling effects. In order to create a box-like Co distribution within a 150 nm thick layer (Fig. 1), ion implantations were performed as a sequence of five different ion energy and fluence combinations that were determined by SRIM¹⁸ simulations. X-ray diffraction (XRD) measurements were performed using filtered Cu-Kα radiation of a PANalytical Empyrean diffractometer. Further microstructure analysis was done by transmission electron microscopy (TEM) measurements using an image-corrected Titan 80–300 microscope (FEI) operated at 300 kV accelerating voltage. The local chemical environment of the implanted Co⁺ within the host lattice was investigated by means of X-ray absorption near-

edge spectroscopy (XANES) and magneto-optical (MO) spectroscopy. Co K-edge XANES spectra were collected in energy resolved fluorescence mode at room temperature, using the Rossendorf Beamline (ROBL, BM-20) at the European Synchrotron Radiation Facility. In order to enhance the signal of the Co⁺-implanted surface region, measurements were performed in one degree grazing incidence geometry. The MO spectra were collected in the transversal Kerr effect (TKE) geometry using the dynamic method in the energy range from 0.5 to 3.5 eV with applied external magnetic field of 3.0 kOe. Magnetic properties of Co⁺-implanted TiO₂ films were determined using a superconducting quantum interference device (SQUID, Quantum Design MPMS XL 7).

III. RESULTS AND DISCUSSION

XRD spectra of as-grown polycrystalline and epitaxial films revealed that both are single phase anatase (Fig. 2). Moreover, for the epitaxial film, only 00/ reflections ($l = 4, 8$) were observed. Rocking-curve (RC) measurements at the anatase (004) reflection indicated a full width at half maximum (FWHM) of 0.81° for the as-grown epitaxial film, confirming out-of plane c-axis texture, i.e., TiO₂(001)||STO(100). Furthermore, single domain TiO₂(100)||STO(001) in-plane order was observed during rotational scans (not shown). After Co⁺-implantation, both polycrystalline and epitaxial films remained mostly in the anatase phase. However, ion implantation decreased the structural quality, which is observed as lowered anatase peak intensities and increased anatase (004) RC FWHM in case of the epitaxial film (inset in Fig. 2(b)). Furthermore, it is found that Co⁺-implantation induces the formation of rutile TiO₂ crystallites in all three as-grown structures. In the epitaxial anatase film, the rutile (111) lattice planes are aligned parallel to the anatase c-axis. A rough estimation on the amount of the ion implantation-induced rutile phases can be made by comparing the peak areas of the anatase and rutile reflections. The rutile-to-anatase ratio was estimated to be around 6% for the TiO₂:Co polycrystalline film, whereas for the TiO₂:Co epitaxial

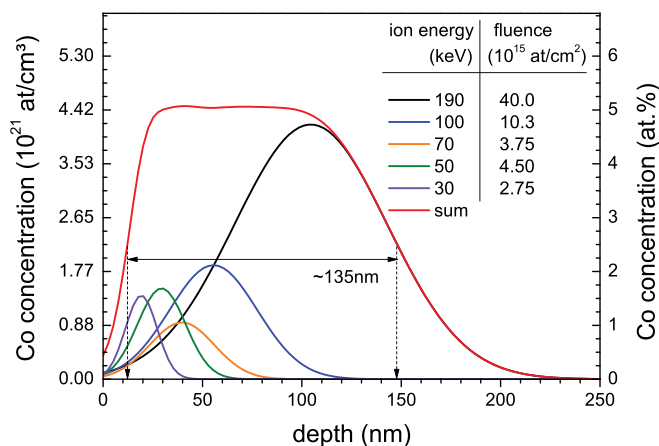


FIG. 1. Depth profiles of Co⁺-implanted into TiO₂ calculated using SRIM. Five different energy-fluence combinations have been used to achieve a box like sum profile.

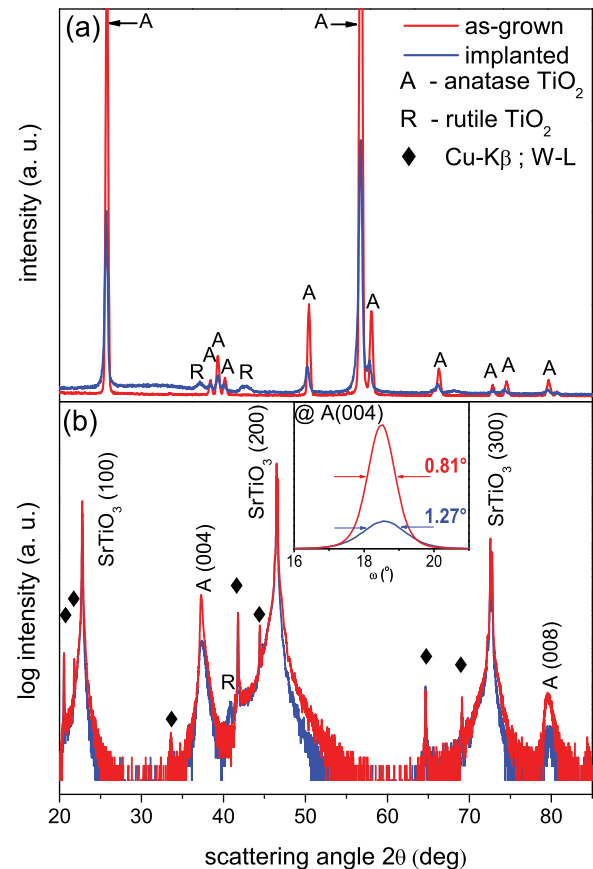


FIG. 2. XRD pattern of as-grown and Co⁺-implanted TiO₂: (a) polycrystalline film in 1° grazing incidence, and (b) epitaxial film in aligned symmetric 2θ-ω geometry. The inset in (b) shows the anatase TiO₂ (004) rocking curves of the epitaxial film.

film, the estimation yielded 0.2% rutile-to-anatase ratio. Furthermore, no other cobalt related secondary phases have been observed by XRD.

The anatase structure of TiO₂ is a metastable phase, which transforms irreversibly to rutile when a sufficient amount energy is introduced into the system.¹⁹ Ion implantation is based on bombarding the host material by highly energetic ions, which leads to energy transfer to the host lattice. The energy, which is transferred to the host lattice is inversely proportional to the ion trajectory length.²⁰ Taking into account, the ion channeling effect during implantation, the ion trajectory length should increase while going from polycrystalline to epitaxial microstructures. The applied tilt of the sample of 10° is not sufficient to fully suppress channeling during implantation. The difference in penetration depths of the implanted Co⁺ can also be seen in the TEM images. Accordingly, the amount of the energy transferred into the host lattice during ion implantation is expected to be higher for the case of the polycrystalline film as compared to the epitaxial film. Thus, the experimental findings regarding to the amount of the implantation-induced rutile phases are consistent with aforementioned mechanistic scenario.

Cross-sectional high-angle annular dark-field (HAADF) scanning TEM (STEM) micrographs of the 5 at. % Co⁺-implanted epitaxial and polycrystalline TiO₂ films are displayed in Fig. 3. Besides, the SrTiO₃ substrate, the overview

images of the $\text{TiO}_2\text{:Co}$ films in (a) and (c) show the unimplanted, as well as the Co^+ -implanted TiO_2 regions. In particular, these STEM micrographs confirm that the implantation profiles end well above the substrate, with slightly different depth profiles for different microstructures. Hence, mixing at the $\text{TiO}_2/\text{SrTiO}_3$ interface and possible long-range ion channeling are avoided. Moreover, clusters with an average diameter of approximately 3 nm and 2.5 nm are observed for the Co^+ -implanted epitaxial and polycrystalline films, respectively. (Figs. 3(b) and 3(d))

SQUID magnetometry revealed the absence of room-temperature FM for all 5 at. % Co^+ -implanted films, independent on their microstructure. A higher paramagnetic response was observed for the Co^+ -implanted epitaxial film as compared to the other films. The blocking temperature (T_B), determined from the zero-field cooling (ZFC) curve of the Co^+ -implanted epitaxial and polycrystalline films, at 15 K and 9 K, respectively, indicates thermally relaxed magnetic interactions, i.e., superparamagnetic behavior. The thermal stability of a magnetic nanoparticle is determined by its volume and its anisotropy energy. T_B can be estimated by $T_B \approx KV/30k_B$, where K is anisotropy energy density, V is the particle volume and k_B is the Boltzmann constant.²¹ Well known candidate phases for the origin of the observed superparamagnetism in the Co-Ti-O material system are hcp-Co ($K = 45 \times 10^4 \text{ J/m}^3$) (Ref. 21) and cubic spinel Co_3O_4 ($K = 9 \times 10^4 \text{ J/m}^3$).²² Using a size of 3 nm of the Co-rich particles as determined for the epitaxial film, the calculation yields blocking temperatures of $\approx 15 \text{ K}$ and $\approx 3 \text{ K}$ for hcp-Co and Co_3O_4 , respectively. Moreover, magnetic field dependent magnetization measurements of both samples below T_B showed a ferromagnetic-like behavior (Fig. 4 inset) below

blocking temperatures, where, for Co_3O_4 , it is expected to be an antiferromagnetic behavior.²³ Therefore, both TEM and SQUID results can be explained consistently by the formation of metallic Co nanoparticles within the TiO_2 matrix. Additionally, the saturation magnetization of the Co^+ -implanted epitaxial and polycrystalline films were found to be 0.16 and 0.14 μ_B per Co atom, respectively (see inset in Fig. 4). By comparison to the room temperature saturation magnetization of bulk hcp Co ($1.7 \mu_B/\text{Co}$),²⁴ it is estimated that, in the epitaxial and polycrystalline samples, less than 10% of the implanted Co atoms are concentrated in metallic nanoclusters. On the other hand, for the Co^+ -implanted amorphous film, only a paramagnetic signal could be detected, indicating the absence of superparamagnetic clusters. The non-existence of macroscopic room temperature FM in all three sample types does not necessarily exclude the presence of substitutional Co_{Ti} , which is thought to give rise to FM according to Refs. 1 and 11, but demonstrates the lack of an appropriate long-range magnetic coupling mechanism in the investigated samples.

Co K-edge XANES spectra of three different Co^+ -implanted TiO_2 microstructures are shown in Fig. 5. The Co K-edge position of a metallic Co foil was used as an energy reference and the edge jump of all recorded spectra was normalized to unity. This allows for a proper comparison with Co, CoO (Ref. 25), and CoTiO_3 (Ref. 26) reference spectra.²⁷ The edge positions of the reference spectra were corrected with respect to metal Co edge position, which is adjusted to the same energy position. The same main Co-K edge position of around 7720 eV was observed for all three $\text{TiO}_2\text{:Co}$ sample types, which is characteristic for Co in (II) oxidation state as can be inferred from the coincidence with the CoTiO_3 and CoO spectra. This indicates that the majority of the implanted Co atoms are indeed oxidized and only a small fraction forms the previously discussed metallic nanoclusters. The main difference in the local environment of Co (II) in CoO and CoTiO_3 is in the oxygen coordination. The oxygen coordination of Co atoms is undistorted and distorted octahedral in CoO and CoTiO_3 , respectively.²⁷ Moreover, Ti in both anatase and rutile TiO_2 also shows distorted octahedral oxygen coordination.²⁸ The similarity of the measured Co-K edges of Co^+ -implanted TiO_2 to that of CoTiO_3 indicates a distorted

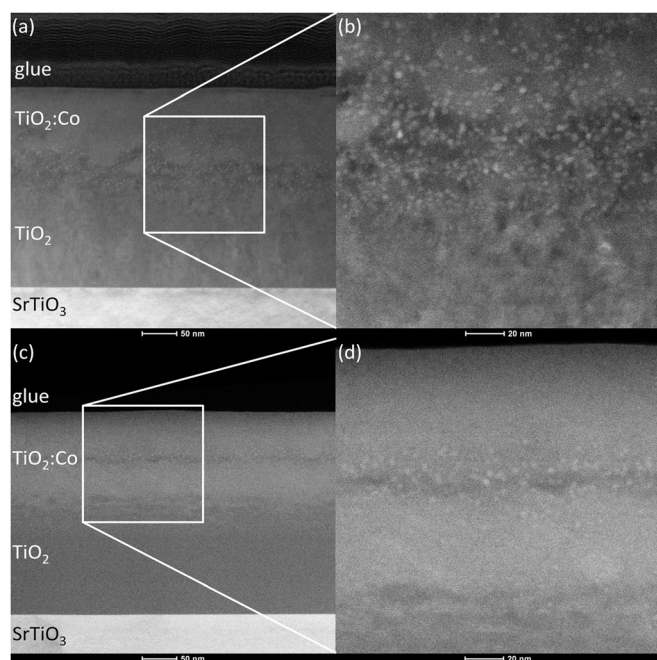


FIG. 3. HAADF STEM of the Co^+ -implanted TiO_2 films: (a) cross-sectional overview and (b) high magnification micrograph of the implanted area of the epitaxial anatase $\text{TiO}_2\text{:Co}$ film. (c) Cross-sectional overview and (d) high magnification micrograph of the implanted area of the polycrystalline anatase $\text{TiO}_2\text{:Co}$ film. Nanoclusters appear as bright contrast in (b) and (d).

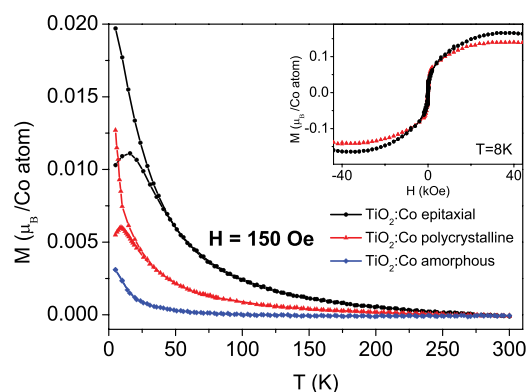


FIG. 4. Temperature dependent magnetization curves (zero-field cooled/field-cooled) of Co^+ -implanted TiO_2 films with different microstructures under applied magnetic field of 150 Oe. The inset shows field dependent magnetization below the blocking temperatures.

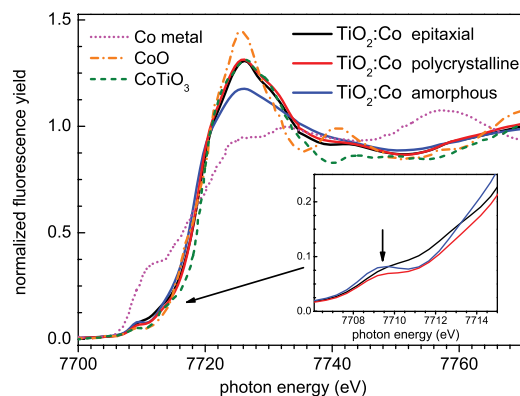


FIG. 5. Co K-edge XANES spectra (normalized) of Co^+ -implanted epitaxial anatase, polycrystalline anatase and amorphous TiO_2 films together with Co K-edge spectra of Co foil, CoO (Ref. 25) and CoTiO_3 .²⁶

octahedral oxygen coordination for the epitaxial and polycrystalline structures. Thus, the observed Co-K edge spectra are assigned to substitutional Co_{Ti} in the TiO_2 lattice, which is in agreement with previous reports.^{29,30} The pre-peak feature at around 7710 eV shown in the inset of Fig. 5 is related to the mixing of Co 3d and O 2p states and can be used to separate oxidic Co environment from metallic Co.²⁷ It is found that the pre-peak feature shape correlates with the presence of metallic Co clusters, i.e., it is most pronounced in case of the amorphous film where no Co cluster formation is observed, while an increase of the pre-peak feature broadening is observed for the polycrystalline and epitaxial samples, suggesting a dependence on nanocluster size and concentration. Besides, the difference in the pre-peak region, the intensity of the white line at 7726 eV is significantly lower in case of the Co^+ -implanted amorphous film compared to the two crystalline samples. This behavior has been reported to be a signature of the prevalent tetrahedral local symmetry of Co, contrary to the octahedral environment (Fig. 5).³¹

Complementary characterization of the Co^+ -implanted TiO_2 films was done by MO TKE measurements at room temperature, where all films are in paramagnetic state. While no TKE signal could be observed for the $\text{TiO}_2\text{:Co}$ amorphous sample, the Co^+ -implanted polycrystalline and epitaxial anatase TiO_2 films showed a significant TKE signal (Fig. 6). The observed optical transitions for the polycrystalline and

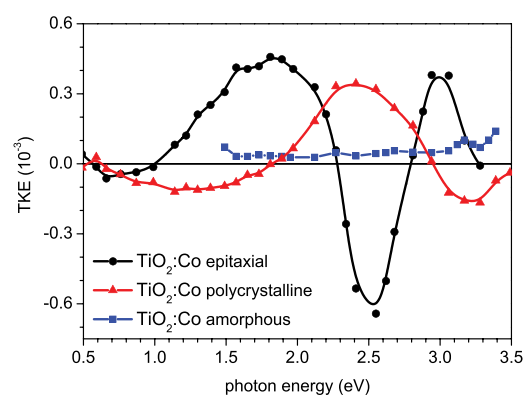


FIG. 6. Room temperature magneto-optical (MO) transversal Kerr effect (TKE) spectra of Co^+ -implanted TiO_2 films with different microstructures.

the epitaxial films coincide with intraionic transitions of Co (II) in octahedral oxygen coordination, which are located at around 0.9, 1.8, and 2.5 eV.^{32,33} The transitions observed around 3.1 eV are assigned to the band gap of the TiO_2 .³⁴ The MO TKE spectrum of the Co^+ -implanted epitaxial film resembles previously published data obtained from epitaxial anatase $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\lambda}$ films on LaAlO_3 (100) substrate prepared by DC magnetron sputtering.³⁵ Thus, TKE measurements confirm the (II) octahedral oxygen coordination of Co, observed from XANES measurements for the Co^+ -implanted crystalline films. The approximately five times lower TKE signal of the present data than reported in Ref. 25, and the shift of the MO spectral features of the polycrystalline film as compared to the epitaxial film suggest a competition between Co incorporation into the host lattice and secondary phase formation. Slightly different Co environment, different rutile-to-anatase ratios and metallic cluster formation may affect resulting shape and intensity of the recorded MO spectra.

IV. SUMMARY

TiO_2 films with different microstructures were implanted with 5 at. % Co^+ . The presence of substitutional Co_{Ti} in the Co^+ -implanted polycrystalline and epitaxial films was confirmed by a combination of XANES and magneto-optical spectroscopy methods. No long-range ferromagnetic ordering at room temperature has been observed for any of the three investigated $\text{TiO}_2\text{:Co}$ structure types. The existence of metallic Co nanoclusters in epitaxial and polycrystalline films giving rise to superparamagnetism at low temperatures was revealed by TEM and SQUID magnetometry. The largest average cluster size and concentration were observed for the Co^+ -implanted epitaxial anatase TiO_2 , whereas amorphous TiO_2 shows paramagnetic behavior after Co^+ -implantation, indicating the absence of Co clusters. Despite the cluster formation, high temperature ferromagnetism is absent and the substituting Co atoms are paramagnetic. This indicates that only the incorporation of the dopant within the host lattice cannot satisfy the requirements to achieve ferromagnetism. On the other hand, absence of defect-induced magnetism can be attributed to insufficient amount of defects within all of the $\text{TiO}_2\text{:Co}$ microstructures.³⁶

The results demonstrate that the initial microstructure of TiO_2 plays an important role for its magnetic properties induced by Co-doping via ion implantation. Increasing the structural ordering from amorphous to polycrystalline anatase and to epitaxial anatase promotes the formation of Co nanoclusters, which counteracts the synthesis of $\text{TiO}_2\text{:Co}$ based DMS materials. Therefore, future studies should focus on suppressing of Co cluster formation, which may be achieved by a further systematic variation of the initial TiO_2 microstructure.

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