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Impact of vacuum thermal treatments on the structure and magnetic properties of titanium oxide films doped with Co

L A Balagurov[1], S O Klimonsky[1], S P Kobeleva[1], A S Konstantinova[2], A F Orlov[1], N S Perov[2], A Sapelkin[3] and D G Yarkin[1]

[1] Institute of Rare Metals, Moscow, 119017, Russia
[2] Department of Physics, Moscow State University, Moscow, 119992, Russia
[3] Department of Physics, Queen Mary, University of London, London E1 4NS, UK

E-mail: rmdp@girmet.ru (A F Orlov)

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Abstract

The structure and magnetic properties of different titanium oxide films doped with magnetic impurities are investigated both in the as-deposited state and after thermal treatments in a vacuum. The samples were characterized by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS) and vibrating sample magnetometry. In the as-deposited films, ferromagnetism was shown to be caused by the formation of magnetic clusters during the deposition. Heating of $Ti_{1-x}Co_xO_{2-\delta}$ films in a vacuum up to high temperatures and the following quenching thereof result in partial dissolution of the clusters with the magnetic ions being incorporated into the matrix. The low-temperature vacuum annealing leads to an increase of weak ferromagnetism in the semiconductor solid solution.

1. Introduction

Numerous studies of oxide magnetic semiconductors have so far been concerned with materials in magnetic clusters (for instance, [1–5]). However, it is clear that clustering of magnetic impurities cannot ensure the effective polarization of charge carriers in a semiconductor that is necessary for spintronic applications. Thus, the task is to achieve charge-carrier mediated *intrinsic* ferromagnetism in a material by creating a single-phase structure with a magnetic impurity incorporated into the lattice. One of the ways of achieving this is based on the features of the phase diagram of Ti–M–O systems, where M is a magnetic impurity. Binary phase Ti–Co and Ti–Fe diagrams indicate rather poor solubility of Co and Fe impurities in the lattice of α-Ti with the limits of 0.8 at.% and 0.5 at.%, respectively. At the same time the above impurities dissolve much better in the high-temperature β-Ti phase: 12 at.% and 20 at.%, respectively. A detailed ternary diagram of oxygen with the above metals is not available, but the existing

data indicate that solubility for low- and high-temperature phases does not change in general. Therefore, one can expect an adequate incorporation of impurity into the oxide if the high-temperature phase is obtained under normal conditions. Indeed, the increase in the anatase lattice parameter was observed after annealing of $Ti_{0.93}Co_{0.07}O_{2-\delta}$ film at up to 950 °C in an argon atmosphere [6].

Another way to prepare a single-phase magnetic oxide semiconductor [7] is via the creation of an oversaturated vacancy concentration in dielectric M:TiO_2 films as a result of low-temperature vacuum annealing of the films after deposition.

In this paper we report an investigation of the impact of high- and low-temperature vacuum treatments on the structure and magnetic properties of titanium oxide films doped with Co (as well as, partially, Fe and V).

2. Experimental details

The $Ti_{1-x}M_xO_{2-\delta}$ films were deposited by rf magnetron sputtering of metal alloy targets in an Ar–O_2 mixture at an oxygen partial pressure of 2×10^{-6}–2×10^{-4} Torr on matching $SrTiO_3$(001) and $LaAlO_3$(001) substrates. The substrate temperature and the growth rate were 550 °C and 0.01–0.05 nm s^{-1}, respectively. Most of the results reported here are for films 0.2–0.3 μm thick. However, for detailed compositional analysis with energy-dispersive x-ray spectroscopy, thicker films (1–2 μm) had to be used. Electrical, structural and magnetic measurements were made on films both before and after thermal processing. The standard four-terminal geometry was used to measure the electrical resistivity ρ. The magnetic characteristics of the films were obtained by vibrating sample magnetometry. The structure of the as-deposited as well as of the processed films was investigated with using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS). To exclude possible surface oxidation in air, all XPS measurements were performed after etching of the films immediately in the chamber of the photoelectron spectrometer.

3. Results and discussion

The resistivity of as-deposited films was found to lie in the range of 10^{-4}–10^6 Ω cm, depending on the growth rate and the content of the gas mixture. The film structure (figure 1) changed with the decrease of resistivity (and the oxygen concentration) from a mixture of anatase and rutile M:TiO_2 to a single-phase tetragonal anatase, further to cubic monoxide M:TiO and finally to the amorphous metal Ti–M. TiO_2 anatase and rutile films were found to be semiconducting: TiO is semi-metallic and amorphous Ti films show metallic conductivity. TiO_2 films doped with Co or V revealed n-type conductivity whereas Fe doping resulted in p-type conductivity.

At room temperature, as-deposited $Ti_{1-x}Co_xO_{2-\delta}$ films exhibit ferromagnetic behaviour with a clearly pronounced magnetic hysteresis loop when the film resistivity changes by more than four orders of magnitude (figure 2). At a Co content of 8 at.%, the carrier densities at the limits of the doping range of the ferromagnetic phase were 2×10^{18} and 3×10^{22} cm^{-3}, while the carrier mobility is 0.3–0.5 cm^2 V^{-1} s^{-1}. At a Co content of 4 at.%, the minimum carrier density corresponding to the onset of ferromagnetism is higher (6×10^{18} cm^{-3}). As-deposited films doped with 8 at.% Fe reveal room-temperature ferromagnetism only at a resistivity below 10 Ω cm, while the films doped with 3–10 at.% V show a ferromagnetic ordering even at 10^6 Ω cm.

The room-temperature ferromagnetism of as-deposited $Ti_{0.92}Co_{0.08}O_{2-\delta}$ films in the charge-carrier concentration range of 2×10^{18}–3×10^{22} cm^{-3} was found to result from the formation of Co-enriched ferromagnetic clusters amounting to a certain critical size [8]. The minimum size of such ferromagnetic clusters is the order of a few nanometres [4]. At a low

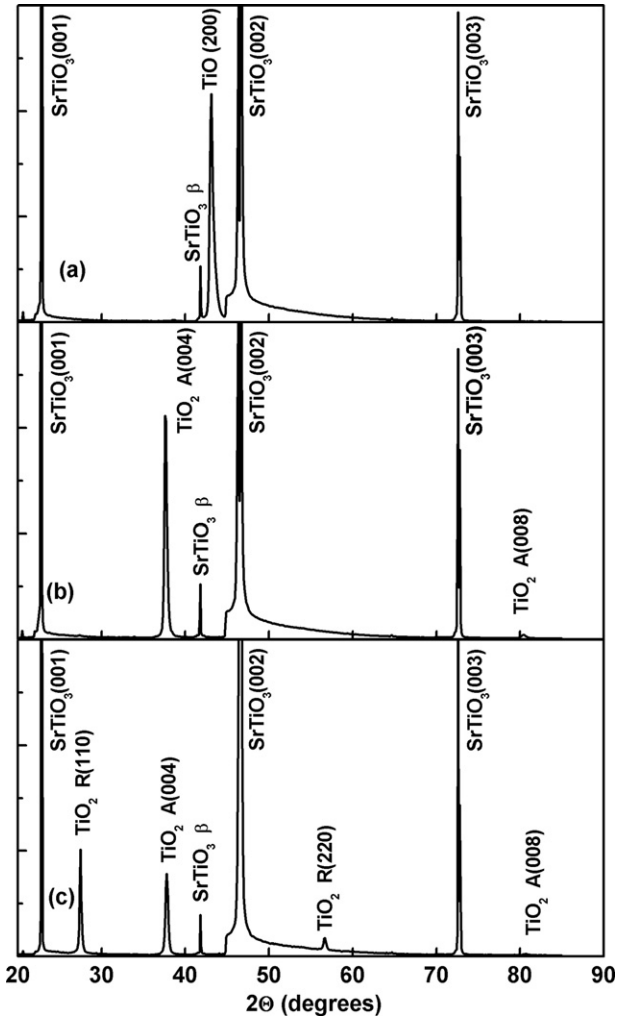

Figure 1. X-ray diffraction patterns for $Ti_{0.92}Co_{0.08}O_{2-\delta}$ films deposited on $SrTiO_3(100)$ substrates: (a) cubic TiO structure, (b) tetragonal anatase (A) TiO_2 structure, (c) a mixture of anatase and rutile (R) TiO_2 phases.

carrier concentration (and hence at a low concentration of oxygen vacancies) the clusters did not reach the critical size during the film deposition. At a carrier concentration above 3×10^{22} cm^{-3} the $Ti_{1-x}Co_xO_{2-\delta}$ films did not reveal the ferromagnetic ordering either (figure 2). The characteristic features of IR and Raman spectra (not shown) point to an amorphous structure for such films.

After deposition $Ti_{1-x}Co_xO_{2-\delta}$ films with various conductivity values were subjected to either low-temperature vacuum annealing or vacuum quenching from high temperatures. XPS and XAS spectra were measured for both as-deposited and processed $Ti_{1-x}Co_xO_{2-\delta}$ films to determine the oxidation state of Co dopant in the lattice. Figure 3 shows near edge x-ray absorption fine structure (NEXAFS) at the Co K-edge of various $Ti_{1-x}Co_xO_{2-\delta}$ samples. Curve (a) depicts x-ray absorption in the highly resistive $Ti_{0.92}Co_{0.08}O_2$ film. In comparison to the reference signal [9], the shape of the spectrum indicates the existence of just the Co^{2+} oxidation

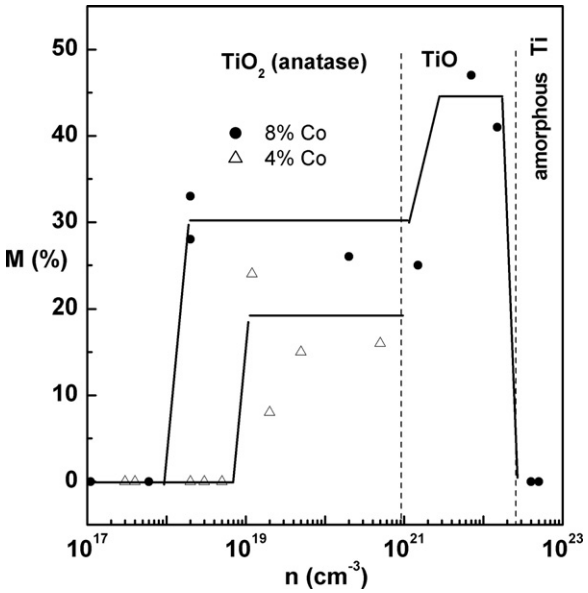

Figure 2. Dependence of relative remanent magnetization M_0 in a zero field on the carrier density n for $Ti_{1-x}Co_xO_{2-\delta}$ films with a Co content of 8 at.% and 4 at.%.

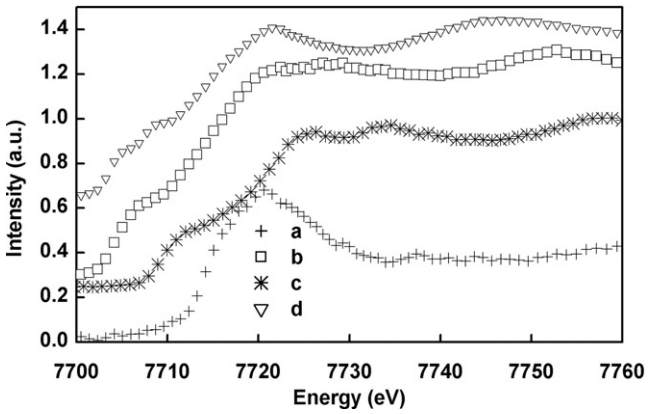

Figure 3. Co K-edge NEXAFS spectrum for various $Ti_{0.92}Co_{0.08}O_{2-\delta}$ films: (a) as-deposited highly resistive (10^6 Ω cm) film, (b) as-deposited film with resistivity of 10^{-1} Ω cm, (c) vacuum-quenched from 950 °C film, (d) amorphous film.

state in the film. The above observation is supported by XPS data: just a single Co $2p_{3/2}$ line is seen in the spectrum (curve (a) in figure 4) with a binding energy of 781.3 eV corresponding to the oxidized Co^{2+} state. This film does not reveal any room-temperature ferromagnetism. For the as-deposited ferromagnetic $Ti_{0.92}Co_{0.08}O_2$ film with a resistivity of 10^{-1} Ω cm both the shoulder in the NEXAFS signal and the spectral shape (curve (b) in figure 3) evidence the existence of Co clusters. Therefore, it could be concluded that ferromagnetism exists in those as-deposited crystalline films which contain Co clusters. Besides, the charge carrier concentration, i.e. the concentration of free oxygen vacancies in the film, should be high enough to ensure diffusive growth of impurity clusters up to their critical size.

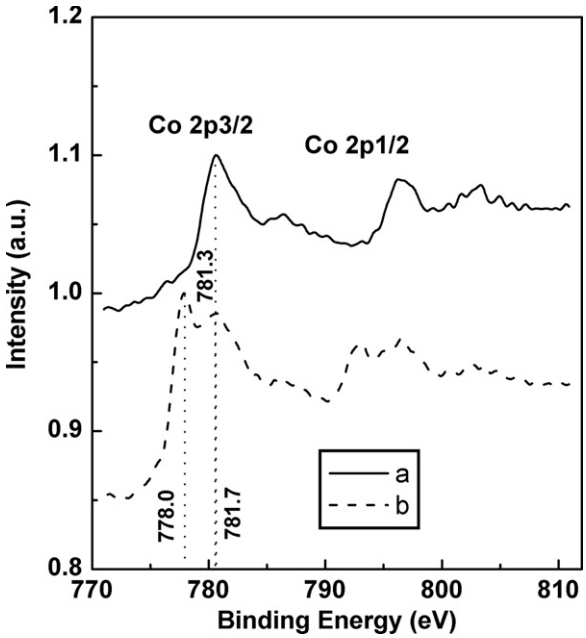

Figure 4. Co 2p core level XPS spectra for: (a) as-deposited $Ti_{0.92}Co_{0.08}O_2$ film with the resistivity of 10 Ω cm and (b) the same film after vacuum quenching from 950 °C.

The XAS results of the amorphous Ti–Co–O film (curve (d) in figure 3) and XPS measurements thereof (not shown) reveal Co clusters in the film. Nevertheless, such films do not demonstrate any ferromagnetic ordering at room temperature; the reason may be their amorphous structure.

Recently [6, 7], the impact of high- and low-temperature annealing on the state of Co-doped titanium oxides has been demonstrated. An increase in the oxide lattice parameter of $Ti_{0.93}Co_{0.07}O_{2-\delta}$ film after its annealing in argon at up to 950 °C was discovered [6]. This was interpreted as a means to incorporate Co impurity into the oxide lattice. The ferromagnetic state was observed for highly resistive $Ti_{1-x}Co_xO_{2-\delta}$ films after vacuum annealing at 450 °C for 1 h [8]. In the present paper we report the changes in structural and magnetic properties of $Ti_{1-x}Co_xO_{2-\delta}$ films taking place under similar vacuum processing conditions.

Figure 5 demonstrates the shift in position of the (004) line in the XRD signal of anatase $Ti_{0.92}Co_{0.08}O_2$ film after high-vacuum annealing at 950 °C for 30 min followed by slow cooling. The lattice parameter is decreased, probably due to the augmentation of the vacancy concentration corresponding to the observed decrease in film resistivity. Besides, the high-temperature rutile phase is partially preserved under slow cooling of the sample to room temperature after annealing. The annealing does not appreciably change the value of the magnetization of the film. Rapid vacuum quenching of anatase films from 950 °C leads to the retention of the rutile phase, whereas the same quenching of the as-deposited rutile films results in a small (0.06 at.%) increase in the lattice parameter. Such a small change in the lattice parameter after the quenching could be a result of two competing processes: the decrease of the lattice parameter due to the augmentation of vacancy concentration and its increase due to partial migration of the impurity atoms from clusters into a solid solution. The latter agrees with the results of XAS (curve (c) in the figure 3) and XPS (figure 4, curve (b)) which indicate that after quenching of $Ti_{0.92}Co_{0.08}O_2$ films from the area of the β-Ti phase the Co impurity

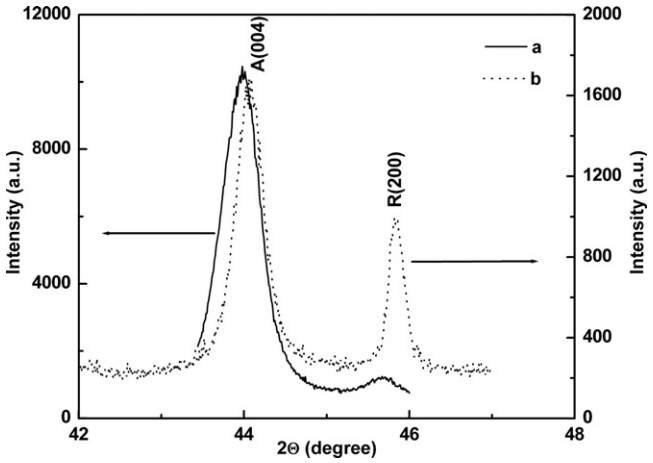

Figure 5. XRD of anatase $Ti_{0.92}Co_{0.08}O_{2-\delta}$ film in the area of the (004) line: (a) as-deposited film and (b) the same film vacuum-annealed at 950 °C and cooled slowly.

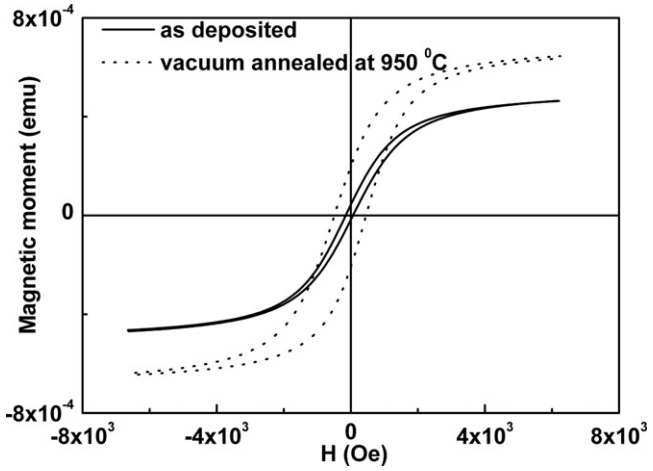

Figure 6. Room-temperature magnetization versus magnetic field curves for $Ti_{0.92}Co_{0.08}O_2$ film in the as-deposited state and after vacuum quenching from 950 °C.

is present in clusters as well as in the matrix. In figure 4 two spectral lines of Co $2p_{3/2}$ with maxima at 781.7 and 778.0 eV correspond to oxidized Co^{2+} and metallic Co^0, respectively.

High-temperature vacuum quenching of $Ti_{1-x}Co_xO_{2-\delta}$ films results in a moderate decrease of the level of magnetization of the material from 1.4 down to 1.1–1.0 μ_B/at. Co and a sharp decrease in the coercivity (figure 6). The decrease of magnetization is possibly caused by the partial transition of the magnetic impurity from clusters into the solid solution. We also note that the coercivity reduces simultaneously with decreasing lattice imperfection.

The low-temperature (450 °C) vacuum annealing of as-deposited highly resistive $Ti_{1-x}Co_xO_{2-\delta}$ films leads to the emergence of a magnetic ordering in the material without Co clustering with a magnetization level of 0.2–0.4 μ_B/at. (figure 7). However, unlike the results reported [7], the charge carrier concentration in our experiments increased under low-temperature vacuum annealing. Thus, we suggest that in such a case the joint spin orientation process in the material is supported by the exchange interaction via charge carriers.

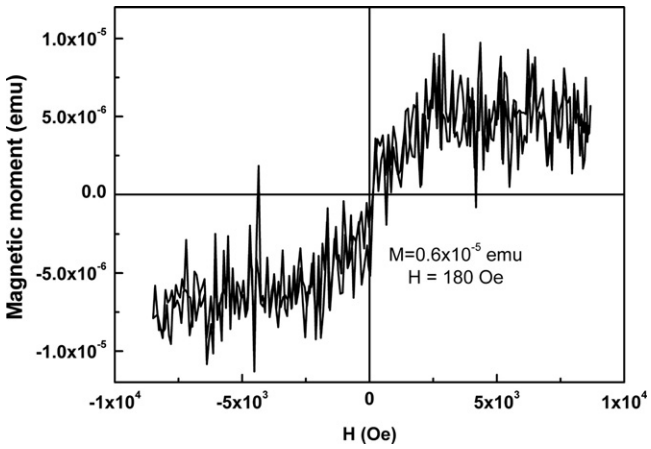

Figure 7. Room-temperature magnetization versus magnetic field curve for $Ti_{0.96}Co_{0.04}O_2$ film after vacuum annealing at 450 °C.

4. Conclusion

In summary, the structural and magnetic properties of different titanium oxide films doped with magnetic impurities have been investigated both in the as-deposited state and after thermal treatments in a vacuum. The ferromagnetism in the as-deposited films was shown to be caused by the formation of impurity clusters during the deposition process. The vacuum quenching of the films from the β-Ti phase results in partial transition of a magnetic impurity from clusters into the matrix. Low-temperature vacuum annealing leads to an increase of weak ferromagnetism in the semiconductor solid solution. The investigation of structural and magnetic properties of the Ti–V–O system in relation to its phase diagram will be continued.

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