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High-temperature ferromagnetism in epitaxial TiO_2 film implanted with cobalt impurity at elevated temperature

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It is shown that implantation of Co^+ ions with an energy of 40 keV and a high dose of $1.25 \cdot 10^{17}$ ion/cm^2 into a thin epitaxial TiO_2 film heated to 873 K induces ferromagnetism with a Curie temperature above room temperature. According to the analysis of presented experimental data, the observed ferromagnetism is mainly due to the formation of cobalt nanoparticles of about 30 nm in size in the implanted TiO_2 film.

Keywords: ion implantation, titanium dioxide, diluted magnetic oxide semiconductors, oxygen vacancies, non-volatile memory.

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The processes of resistive switching in oxides, which are caused by diffusion and ordering of oxygen vacancies in an electric field, are of great current interest. Special attention is paid to titanium dioxide (TiO_2), since a new passive element (memristor) has been produced based on it in 2008 [1]. At the same time, it was demonstrated in [2] that doping of this oxide semiconductor with a magnetic cobalt impurity leads to the emergence of room-temperature ferromagnetism. Thus, magnetically diluted TiO_2 has potential for application not only in non-volatile memory, but also in semiconductor spintronics.

The ion implantation method is used widely [3–5] to produce TiO_2 with a magnetic cobalt impurity. It was demonstrated that the magnetic phase composition and, accordingly, the magnetic properties of TiO_2 with implanted cobalt depend significantly on the ion irradiation modes, the degree of crystallinity, the structural type (anatase or rutile), and even the shape of the irradiated oxide substrate (film, single crystal). Ferromagnetism in TiO_2 implanted with cobalt may be observed both due to the magnetic ordering of magnetic Co^{2+} ions incorporated into the oxide lattice sites and due to the formation of nanosized particles of magnetic impurity cobalt. The present study is the first to examine high-dose cobalt ion implantation into an epitaxial TiO_2 film with a rutile structure at an elevated temperature of the irradiated film. The aim of the study was to establish the nature of high-temperature ferromagnetism observed in the implanted TiO_2 film. In addition to measuring the magnetic properties of the implanted film, we investigated the depth profiles of concentration and valence state of the cobalt impurity, as well as the elemental composition and surface morphology of the irradiated TiO_2 film.

A thin (150 nm) TiO_2 film with a rutile structure was synthesized on a (1102)-oriented (R-cut) corundum (Al_2O_3) substrate by reactive magnetron sputtering followed by annealing in air at $T = 1073$ K for 60 min. It was irradiated with Co^+ ions with an energy of 40 keV and a dose of $1.25 \cdot 10^{17}$ ion/cm^2 at a substrate temperature of 873 K at the ILU-3 ion accelerator. The ion current density was maintained at 2–3 μA/cm^2. The implanted film surface was imaged with an EVO 50 XVP (Carl Zeiss) scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) studies were carried out in an analytical chamber produced by SPECS GmbH (Germany). The magnetic properties were examined by the vibration magnetometry method with a PPMS-9 system (Quantum Design) within the 5–300 K temperature range and via differential thermomagnetic analysis at 300–1073 K.

We have already established [6] that the crystalline structure of an initially epitaxial thin TiO_2 film gets disordered upon implantation. In addition, reflections in the diffraction pattern shift toward lower 2θ values, which may be associated both with the incorporation of impurity cobalt into titanium sites and with the formation of a large number of defects leading to „swelling“ of the film [6].

Figure 1, *a* shows the depth profiles of concentration of structure-forming elements (Ti and O) and the Co impurity in the implanted TiO_2 film determined by analyzing the XPS spectra. The presented data make it evident that the TiO_2 film thickness decreased to 105 nm after implantation, which is attributable to film sputtering in the process of ion irradiation and is consistent with the measurements of height (~ 44 nm) of the step between the irradiated and non-irradiated parts of the sample. In this case, impurity cobalt is concentrated exclusively in the surface layer with a thickness of ~ 30 nm. The radiation dose determined by integrating the experimental impurity distribution profile is $3.21 \cdot 10^{16}$ ion/cm^2. This is significantly lower than the technical value of the radiation dose ($1.25 \cdot 10^{17}$ ion/cm^2). Such a large discrepancy between the implantation dose

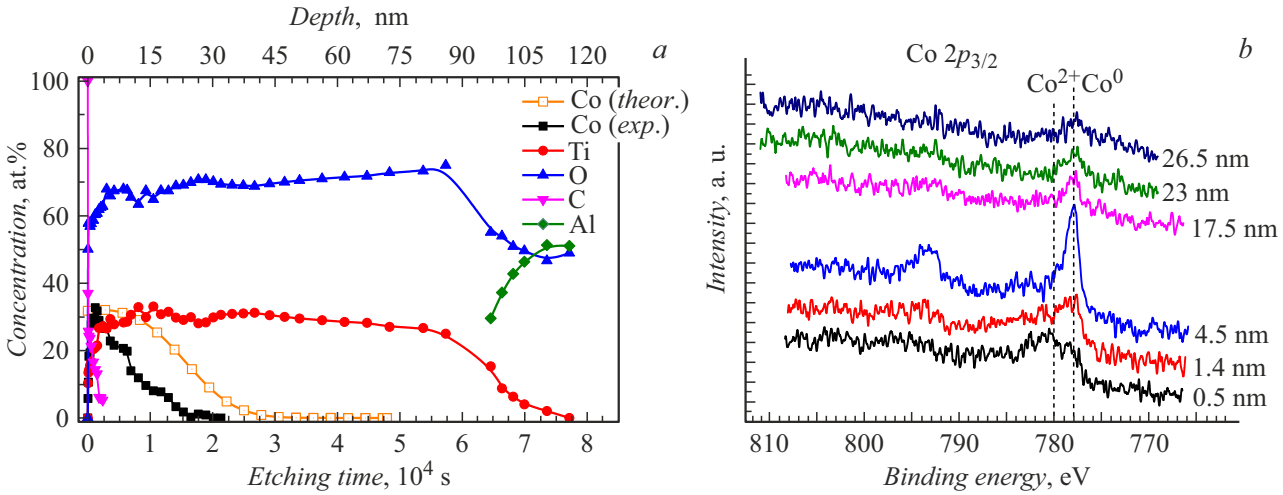

Figure 1. *a* — Depth profiles of Ti, Co, and O distribution; *b* — Co $2p_{3/2}$ XPS spectra recorded at different analysis depths in a thin TiO_2 film implanted with cobalt ions.

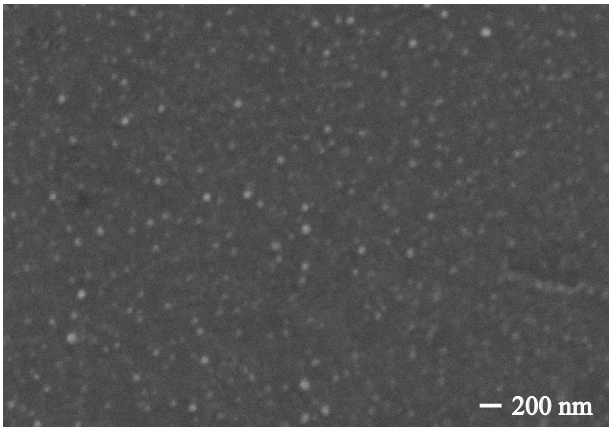

Figure 2. SEM image of the surface of a thin TiO_2 film implanted with cobalt ions.

values is due to two processes: rapid diffusion of the implanted impurity to the film surface and intense sputtering of the surface layer in the case of implantation at high temperatures. Our calculations of the depth profile of cobalt distribution in the TiO_2 matrix (light squares in Fig. 1, *a*) based on the formulae from [7] attest to the fact that impurity atoms are sputtered to a significant degree together with the film material. The integral over the calculated profile is $7.13 \cdot 10^{16}$ ion/cm^2, which is almost 2 times lower than the technical dose value.

High-resolution XPS spectra were measured for the $2p_{3/2}$ electron orbital of cobalt at different impurity depths in order to determine the valence state of cobalt (Fig. 1, *b*). In the surface layer with a thickness of ~ 5 nm, impurity cobalt was found in ionic state Co^{2+}. This is indicative of the presence of cobalt oxide (CoO) on the surface of the irradiated TiO_2 film. At greater depths of analysis, the spectrum component associated with the metallic (Co^0) impurity state is dominant. It is likely that impurity atoms are combined into clusters of metallic cobalt. Such clusters ~ 30 nm in size are indeed seen in the SEM image of the film (Fig. 2) in the form of light spots distributed uniformly over the surface of the film.

The field dependences of magnetization of the studied sample at a measurement temperature of 5 and 300 K are shown in Fig. 3, *a*. Note that the diamagnetic contribution from the unmodified part of the TiO_2 film and the corundum Al_2O_3 substrate was subtracted from the magnetic curves, and the measured magnetic moment values were expressed in Bohr magnetons per impurity atom (with account for the experimentally determined implantation dose). An open magnetic hysteresis loop is seen already at room temperature, which is indicative of ferromagnetic behavior of the sample. The coercive field gest stronger as the measurement temperature decreases (420 Oe at 300 K and 620 Oe at 5 K), whereas the saturation magnetization ($\cong 1.58\,\mu_B$/Co) remains virtually unchanged within the temperature range of 5–300 K. This is indicative of a high Curie temperature in the sample under study, since it is known [8] that the saturation magnetization depends only weakly on temperature far from the critical point. At the same time, a strong temperature dependence of the coercive field indicates that the observed ferromagnetism is of a granular nature. It is known that small magnetic particles pass from the ferromagnetic state to the superparamagnetic one as the temperature increases, thus suppressing the coercive field in the granular system as a whole. The measured saturation magnetization ($\sim 1.58\,\mu_B$) is somewhat lower than the value of $1.72\,\mu_B$ for bulk metallic cobalt [8]. Therefore, only 90 % of impurity cobalt are contained in metal nanoparticles that shape the ferromagnetic properties of the sample. The remaining part (~ 10 %) is in the form of Co^{2+} ions. Some of them are apparently localized in cobalt oxide (CoO) in the surface layer, while the other substitute cationic sites of titanium in the TiO_2 structure in the bulk of the film.

Figure 3, *b* shows the dependences of sample magnetization on temperature in a magnetic field of 5 kOe within the

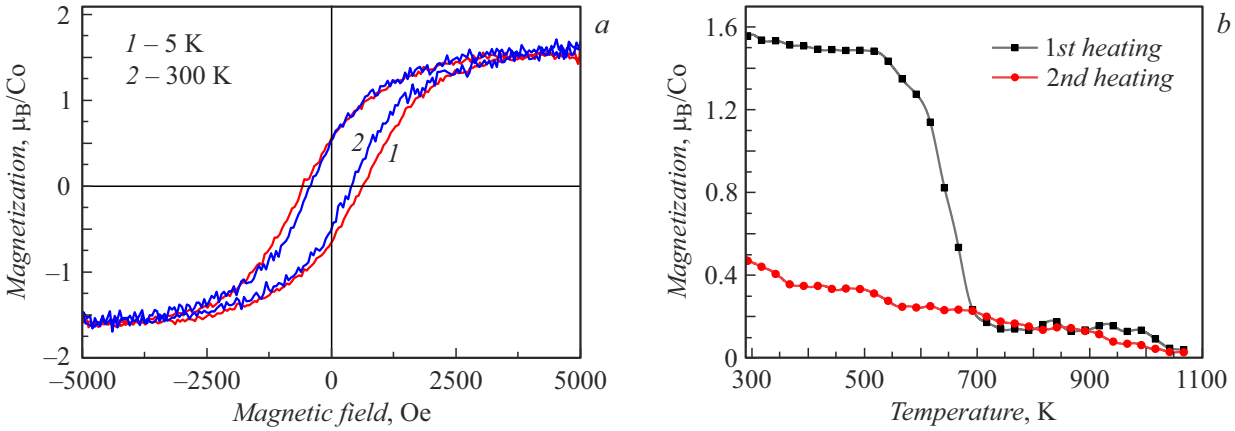

Figure 3. *a* — Magnetic hysteresis loops at temperatures of 5 and 300 K; *b* — temperature dependence of magnetization measured in a 5 kOe field for a thin TiO_2 film implanted with cobalt ions.

300–1073 K range. It can be seen that the magnetization drops sharply at $T = 550–700$ K (squares) as the sample is heated for the first time. Its magnetization was not restored to the original level after cooling, and a featureless temperature dependence of magnetization (circles) was obtained when the sample was heated for the second time. This behavior of thermomagnetic curves is likely to be attributable to the process of oxidation of metallic cobalt nanoparticles during the first heating and their transition to a non-magnetic (at room temperature) CoO phase state.

We note in conclusion that an epitaxial thin TiO_2 film implanted with cobalt ions with an energy of 40 keV and a dose of $1.25 \cdot 10^{17}$ ion/cm^2 at a temperature of 873 K was investigated using a set of experimental methods. It was found that the implanted film has ferromagnetic properties at room and above-room temperatures. The results of X-ray photoelectron spectroscopy and scanning electron microscopy revealed that the observed ferromagnetic response is due to the formation of metallic cobalt nanoparticles with an average size of 30 nm in the irradiated layer of the TiO_2 film. Ferromagnetism vanished at temperatures above 550 K when the film was heated in air, which is attributable to oxidation of cobalt nanoparticles in the TiO_2 matrix.

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Conflict of interest

The authors declare that they have no conflict of interest.

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