Supplementary Materials

Ion-Beam Synthesis of Structure-Oriented Iron Nanoparticles in Single-Crystalline Rutile TiO_2

Iskander R. Vakhitov [1,2,*], Nikolay M. Lyadov [1,2], Vladimir I. Vdovin [3], Anton K. Gutakovskii [3], Vladimir I. Nuzhdin [2], Lenar R. Tagirov [1,2] and Rustam I. Khaibullin [1,2]

[1] Institute of Physics, Kazan Federal University, Kazan 420008, Russia
[2] Zavoisky Physical-Technical Institute, FRC Kazan Scientific Centre of RAS, Kazan 420029, Russia
[3] Rzhanov Institute of Semiconductor Physics, the Siberian Branch of the RAS, Novosibirsk 630090, Russia
*****Correspondence: iskvakhitov@gmail.com

1. SEM study of Fe-ions implanted TiO_2 plates

The surface morphology and content of chemical elements in the TiO_2 samples were studied using an EVO 50 XVP scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer (Oxford, Inca Energy 350). The results of the SEM study of both the original and the (100)-TiO_2 plate heavily implanted with Fe ions are shown in Figure S1. As can be seen from the figure, the surface of the rutile plates after intense ion irradiation remains smooth, without blisters and any neoplasms on the surface. The EDX spectrum confirms the implantation of Fe ions into rutile, and the EDX mapping shows that the iron implant is evenly distributed over the surface of the implanted TiO_2 on a submicron scale. Very similar SEM results were also obtained for the (001)-oriented TiO_2 wafer implanted with Fe ions.

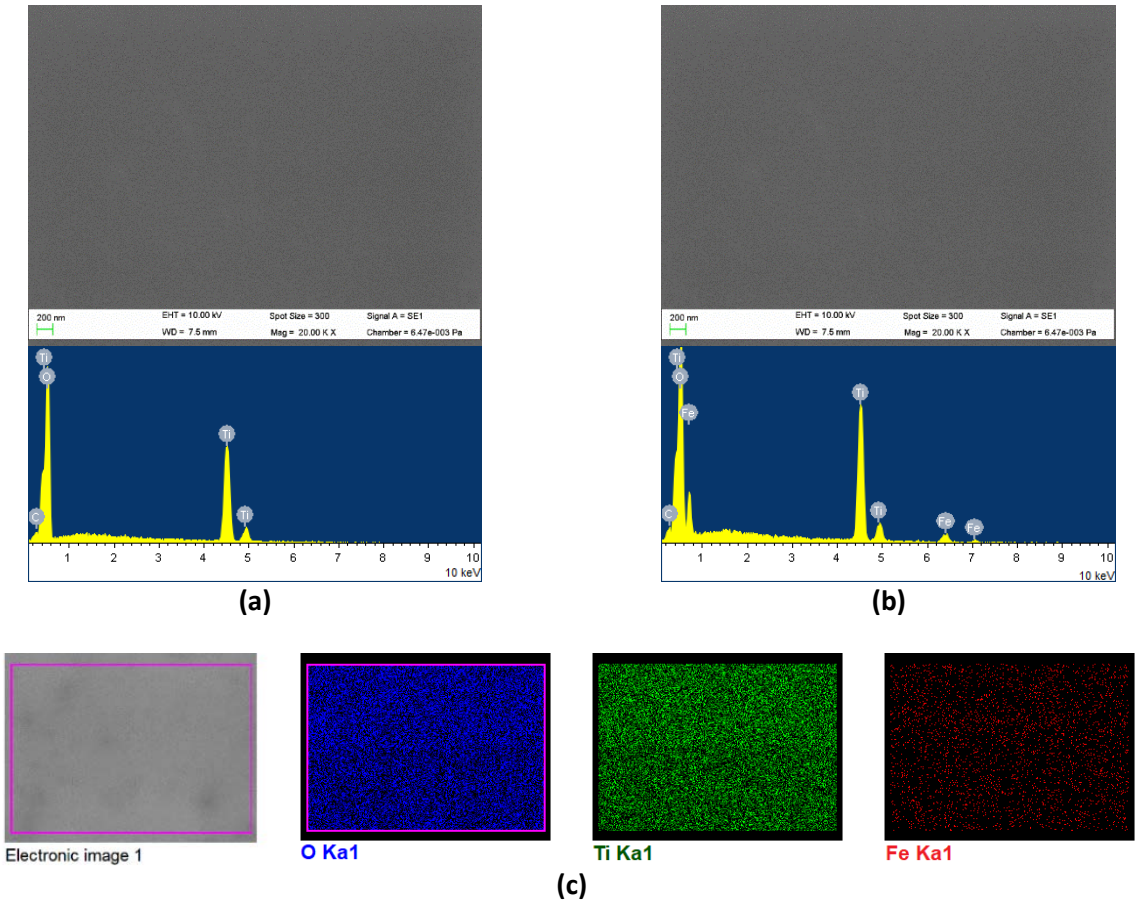
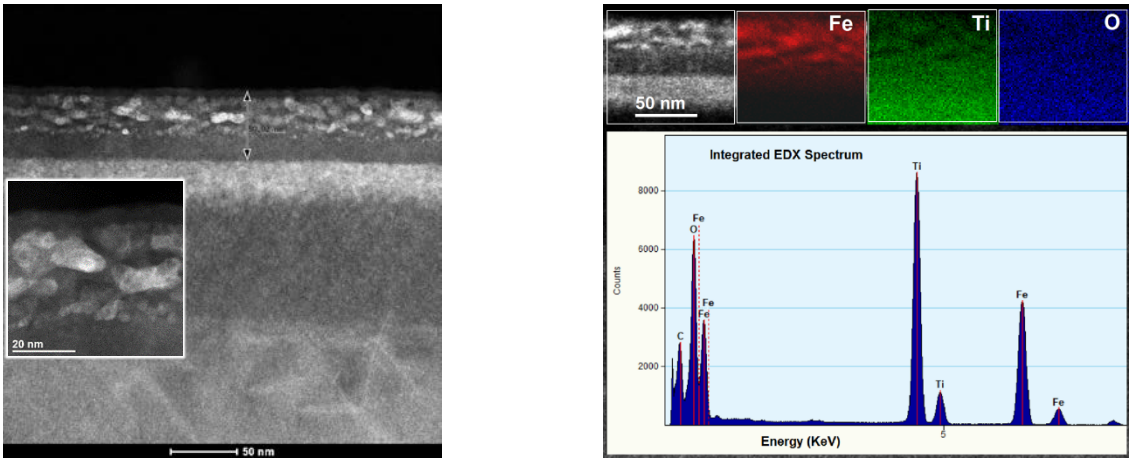


Figure S1. SEM images and EDX spectra of the surface of (100)-TiO_2 plate before **(a)** and after **(b)** implantation of Fe ions with the fluence of 1.5×10^{17} ion/cm^2; **(c)** –EDX elemental mapping of the surface of the Fe-ions implanted (100)-TiO_2 plate on a submicron scale (20,000x magnification).

2. HR TEM and STEM studies of Fe-ions implanted TiO_2

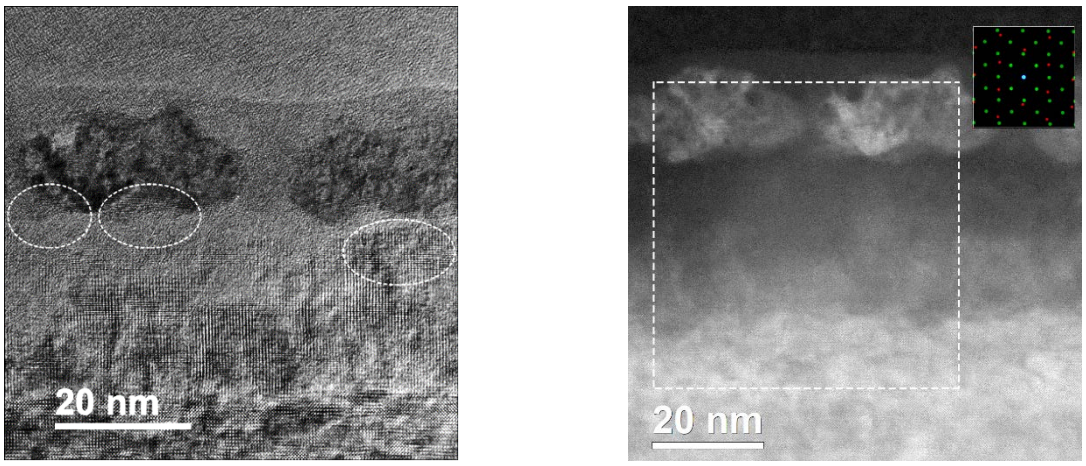
The microstructure and distribution of chemical elements in TiO_2 samples implanted with Fe ions were studied on a transmission electron microscope TITAN-FEI (300 kV) in the high-resolution (HR TEM) and scanning (STEM) modes using an energy-dispersive X-ray (EDX) detector. The results of the STEM study of a (001)-TiO_2 plate implanted with 40 keV Fe^+ ions at a fluence of 1.0×10^{17} ion/cm^2 are shown in Figure S2. It is clearly seen that iron nanoparticles (white spots in the STEM image) are located in a surface layer about 40 nm thick. A change in the size of nanoparticles with respect to the depth of the layer is clearly observed, from large nanoparticles near the surface to small nanoparticles in the bottom part of the layer. The EDX mapping has shown that the iron concentration decreases non-monotonically from the surface to a depth of 70 nm, while the Ti and O content increases.



(a) **(b)**

Figure S2. (a) – Cross-section STEM image and **(b)** – EDX spectrum with EDX elemental mapping of the (001)-face oriented TiO_2 plate implanted with Fe ions to the fluence of 1.0×10^{17} ion/cm^2.

Figure S3 shows HR TEM and STEM cross-sectional images of Fe-ions implanted TiO_2 rutile plate with an another (100) surface orientation. As can be seen in the left panel (a), the surface layer containing Fe nanoparticles is practically amorphous down to a depth of 20 nm, while the areas of the TiO_2 rutile matrix (marked by ellipses) under the iron nanoparticles and in deeper layers remain in the crystalline state. The FFT pattern from a large area (see the inset in panel (b)) indicates the coherent growth of the iron nanoparticles along the specified TiO_2 axes, since the point reflections from the iron nanocrystals have a strict arrangement relative to the rutile reflexes.



(a) **(b)**

Figure S3. (a) – Cross-section HR TEM image of (100)-TiO_2 plate implanted with Fe ions to a fluence of 1.0×10^{17} ion/cm^2; **(b)** – STEM image and FFT pattern (color insert) taken at the same microscopic area of the sample. Here the iron nanoparticles look as dark grey or the white spots in the top region of HR TEM or STEM images, respectively, and the crystalline regions of TiO_2 under the iron nanoparticles are marked by ellipses. The red colored point reflexes of FTT pattern are related to the nanosized crystallites of α-phase metallic iron while the green colored points correspond to reflexes from the TiO_2 matrix of rutile structure.

3. Temperature measurements of magnetic hysteresis loops in TiO_2 plates implanted with 40 keV Fe^+ ions to the different fluences

Magnetic hysteresis loops in the plane of TiO_2 plates with (100) and (001)-face orientations implanted with Fe^+ ions with different flux densities (0.5, 1.0, and 1.5)×10^{17} ion/cm^2 were recorded using a vibrating sample magnetometer (VSM) of Quantum Design PPMS-9 systems. The value of the measured magnetic moment was normalized to a thickness of 40 nm and the sample area about 4 mm^2 to calculate the magnetization of the composite layer containing iron nanoparticles. Figure S4 shows the magnetization curves of TiO_2 implanted with Fe ions at temperatures of 10, 50, 100 and 300 K. It can be seen that TiO_2 wafers implanted with a low energy density of 0.5×10^{17} ion/cm^2 exhibit superparamagnetic behavior over the temperature range 50 – 300 K, and they become ferromagnetic at the lowest temperature of 10 K. Further, with an increase in fluence, iron ions implanted with TiO_2 exhibit a ferromagnetic response over the entire temperature measurement range. The strong dependence of both the coercive field and the hysteresis loops shape on temperature indicates the granular nature of the observed ferromagnetism, and ones is typical for single-domain nanoparticles.

Fe+(100)-TiO_2 **Fe+(001)-TiO_2**

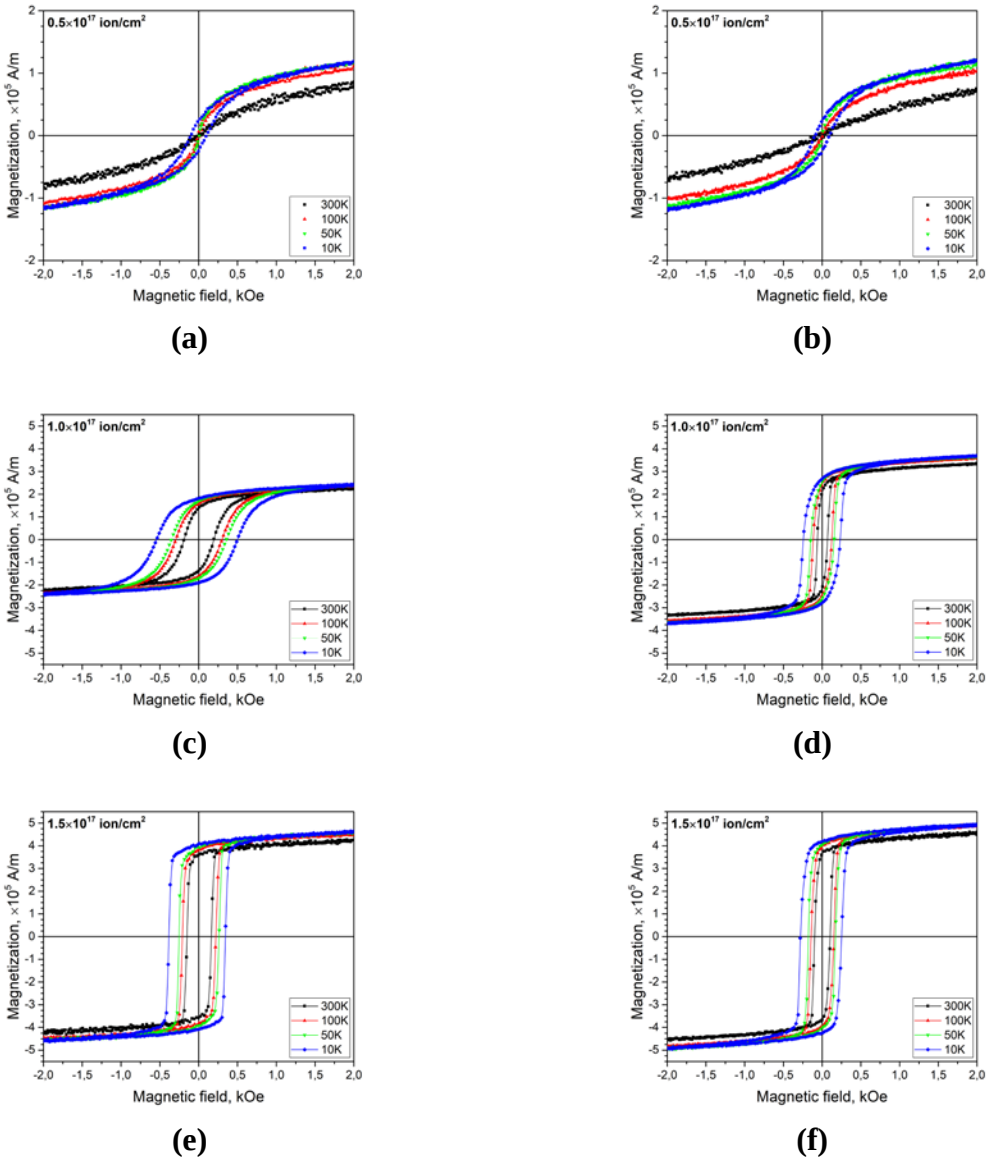


Figure S4. In-plane magnetization curves measured at different temperatures of the (100)-TiO_2 (**a**, **c** and **e**) and (001)-TiO_2 (**b**, **d** and **f**) plates implanted with Fe ions to the fluence of: **(a)**, **(b)** – 0.5×10^{17} ion/cm^2; **(c)**, **(d)** – 1.0×10^{17} ion/cm^2; **(e)**, **(f)** – 1.5×10^{17} ion/cm^2. For all measurements the direction of magnetic field **H** || [010] axis of TiO_2.

4. Observation of in-plane magnetocrystalline anisotropy in Fe-ions implanted TiO_2 plates

The angular dependences of the magnetic hysteresis loops of (100) and (001) face orientated TiO_2 plates implanted with 40 keV Fe^+ ions to the fluences of (0.5–1.5) × 10^{17} ion/cm^2 were studied using an experimental home-made coercive magnetometer. The loops were recorded at room temperature in the in-plane geometry for different crystallographic orientations of the TiO_2 plates with respect to the applied magnetic field (*H*). As was established from the magnetic measurements (see Figure S5), the [010] crystallographic direction in rutile is the easy magnetization axis for both orientations of the implanted TiO_2 plates, and the [001] and [110] directions are the hard magnetization axes in the implanted TiO_2 plates (100)-TiO_2 and (001)-TiO_2, respectively. Note that the in-plane magnetocrystalline anisotropy is much stronger in the (100)-TiO_2 plate than in the (001)-TiO_2 plate implanted with a maximum fluence of 1.5 × 10^{17} ions/cm^2. Planar magnetic anisotropy becomes less pronounced with decreasing the implantation fluence and practically does not observed in the TiO_2 plates implanted with a low fluence of 0.5 × 10^{17} ion/cm^2.

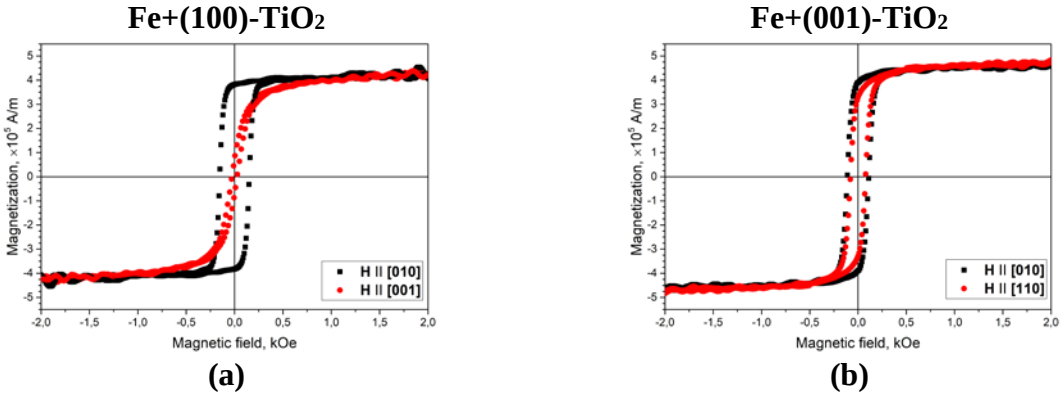


Figure S5. In-plane magnetization curves measured with the magnetic field applied along different crystallographic directions of the TiO_2 plates implanted with Fe^+ ions to the fluence of 1.5×10^{17} ion/cm^2, where **(a)** (100)-oriented TiO_2 substrate and **(b)** – (001)-TiO_2 substrate.