Supplementary Materials

Microstructure and Unusual Ferromagnetism of Epitaxial SnO_2 Films Implanted with Co Ions

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1. SEM study of both as-prepared and Co- (or Ar)-ions implanted SnO_2 films

The surface morphology and chemical element composition of SnO_2 samples were investigated utilizing an EVO 50 XVP scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer (Oxford, Inca Energy 350). The SEM analysis of both the as-prepared and Co-ions implanted SnO_2 film is presented in **Figures S1**. The SEM images clearly illustrate that the surface of the SnO_2 films, upon intense ion irradiation, exhibits pronounced roughness along with the presence of blisters and neoplasms. The EDX spectrum confirms successful implantation of Co ions into the SnO_2 structure, and the EDX mapping reveals a homogeneous distribution of the cobalt implant at the submicron scale across the entire surface of the implanted SnO_2.

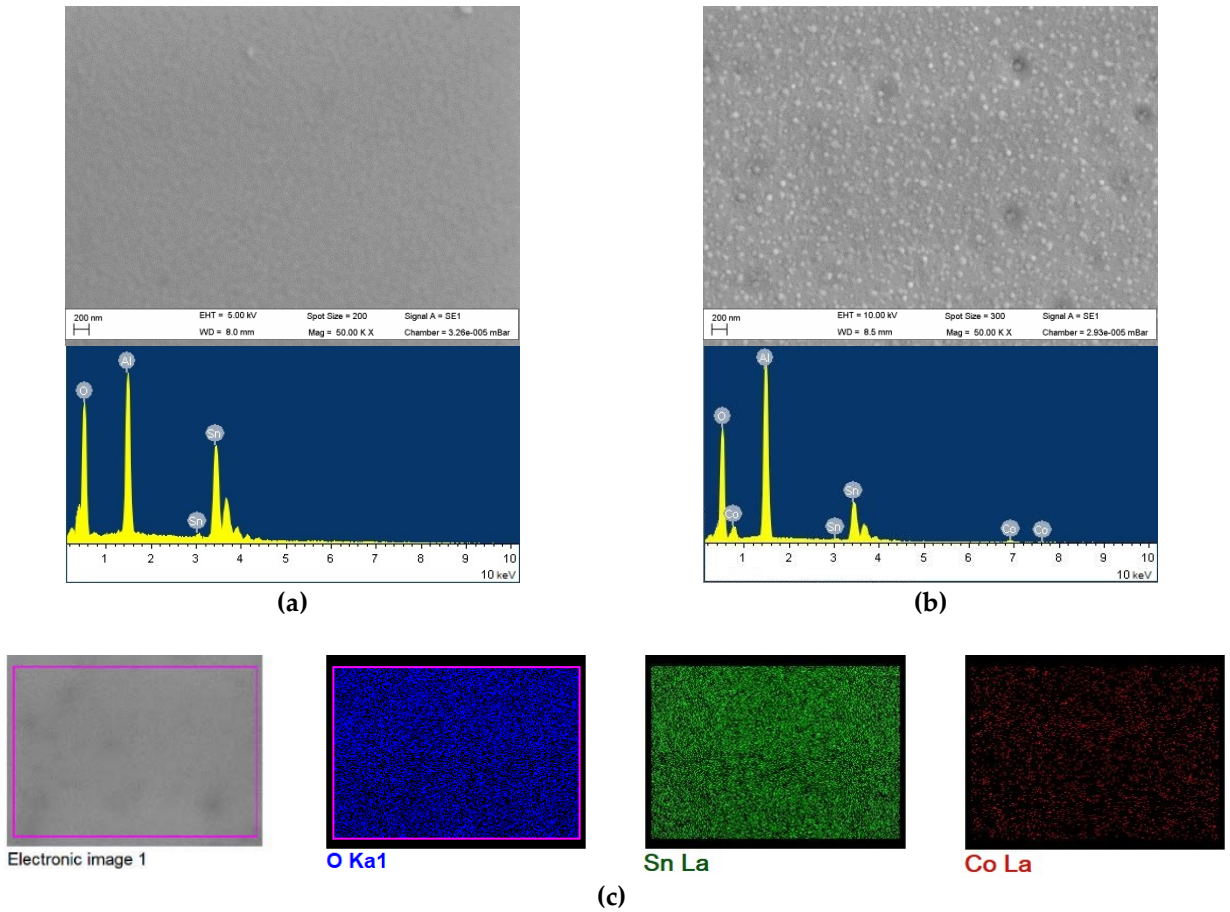
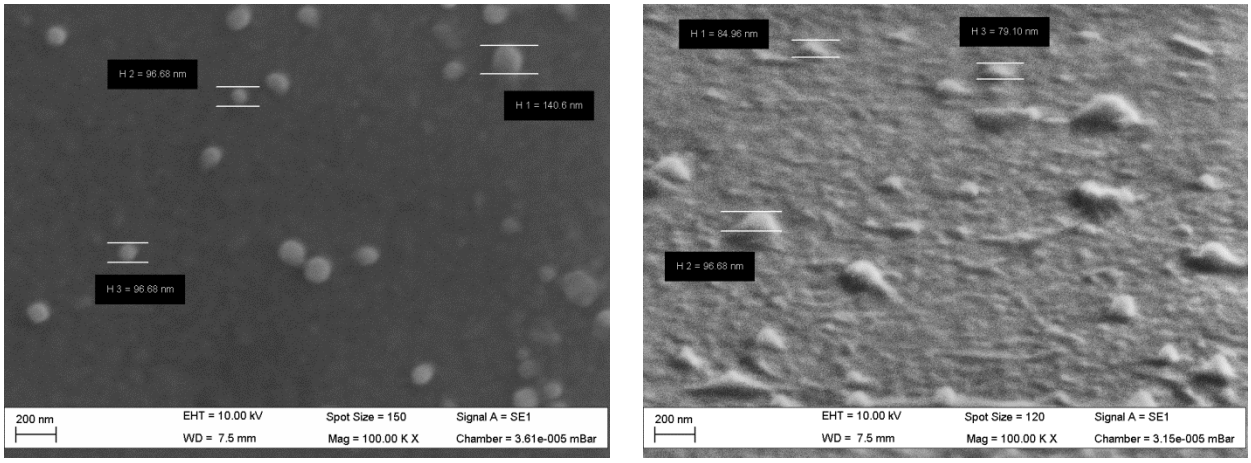


Figure S1. SEM images of the surface of SnO_2 film before **(a)** and after **(b)** implantation with 40 keV Co+ ions to the fluence of 1.0×10^{17} ion/cm^2; **(c)** –EDX elemental mapping of the surface of the Co-ions implanted SnO_2 film at the submicron (20,000x magnification) scale.

The similar picture is taken place in Ar-ions implanted SnO_2 film (see **Figure S2**). Here, the neoplasms with semi-spherical form are also observed on the surface of the film after intense irradiation with argon ions, but their surface density is lower than the density of new formations in films implanted with cobalt ions. Since the EDX spectrum of Ar-ions implanted SnO2 film (not shown) reveals very week energy peaks associated with argon, we can conclude that the most of chemically inert argon leaves the implanted SnO_2 film due to outward diffusion process.

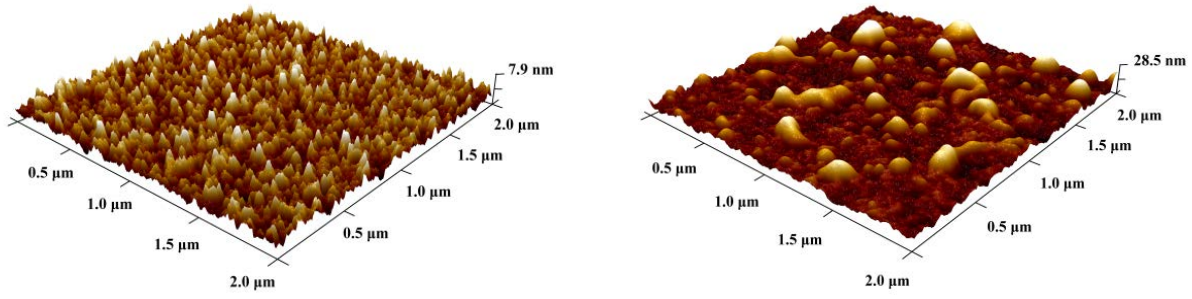


(a) **(b)**

Figure S2. SEM image of the surface of SnO_2 film after implantation with 40 keV Ar+ ions to the fluence of 1.0×10^{17} ion/cm^2 **(a)** and SEM image of same film under 70˚ degrees with respect to electron beam **(b)**.

2. AFM study of both as-prepared and Co-ions implanted SnO_2 films

Atomic force microscopy (AFM) study of the surface morphology of SnO_2 films was performed in additional to SEM study. The Dimension FastScan Bruker AFM has been used for this purpose. An AFM study of the surface morphology of as-prepared SnO_2 films (**Figure S3a**) showed that film surface is quite smooth with a roughness of 5-7 nm. On the contrary, AFM image presented in **Figure S3b** show that large neoplasms (~40-70 nm in sizes) are formed on the surface of the film after high-fluence implantation with Co ions.



(a) (b)

Figure S3. AFM images of the surface of SnO_2 film before **(a)** and after **(b)** implantation with 40 keV Co+ ions to the fluence of 1.0×10^{17} ion/cm^2.

Authors greatly acknowledge Dr. Alexey Rogov (from Kazan Federal University, Russia) for carrying out of the AFM measurements.

3. ^{119}Sn Mössbauer studies of the epitaxial SnO_2 film on C-cut Al_2O_3 substrate before and after Co ions implantation

Room-temperature transmission ^{119}Sn Mössbauer studies were carried out using conventional WissEl spectrometer working in the constant acceleration mode. ^{119m}Sn($CaSnO_3$) source with an activity of about 15 mCi (RITVERC) was used. The spectrometer velocity scale was calibrated using thin metallic iron foil at room temperature. The spectra were least-squares fitted using SpectrRelax 2.1 software [1]. The values of isomer shifts are determined versus center of polycrystalline thin SnO_2 absorber spectrum at room temperature.

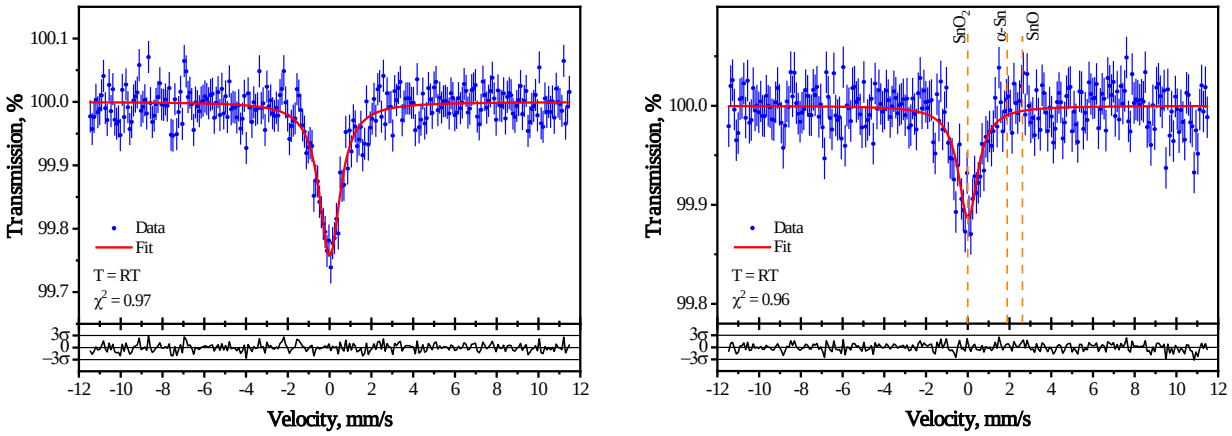


Figure S4. ^{119}Sn Mössbauer spectra of the epitaxial SnO_2 film on C-cut Al_2O_3 substrate before (**a**) and after (**b**) the implantation with 40 keV Co^+ ions with the fluence of 1×10^{17} ions/cm^2. Blue points with statistical error bars represent the experimental spectra, whereas solid red curves – the best-fit results. In panel (**b**) the dashed orange lines show the isomer shift values for tin dioxide (SnO_2), tin monoxide (SnO) α-phase of metallic tin (α-Sn), respectively [2].

The results of ^{119}Sn Mössbauer studies of the epitaxial SnO_2 film on C-cut Al_2O_3 substrate before implantation is shown in **Figure S4(a)**. The spectrum of the film in the initial state was the single absorption line with the isomer shift corresponding to the Sn^{4+} ions in SnO_2. After Co ions implantation, the spectrum did not change qualitatively (**Figure S4(b)**). It should be noted that within the experimental signal-to-noise ratio the additional components corresponding to the tin ions in other states were not observed. It proves that the Co ions implantation did not notably affect the valence state of tin atoms in the implanted SnO_2 film.

4. High-resolution X-ray photoelectron spectra (XPS)

High-resolution XPS spectra were taken at room temperature by using a Phoibos 150 hemispherical energy analyzer (SPECS GmbH, Berlin, Germany). The obtained results were analyzed using CasaXPS software [3]. The experimental data both for as-prepared and Co-ions implanted SnO_2 films are depicted in **Figure S5.** It was established that the valence states of tin and oxygen atoms are preserved under the Co ions implantation and the XPS peak positions correspond to Sn^{4+} and O^{2-} states. At the same time, Co implant was found in the mixed valence state: either in the form of metal atom Co^0 or Co^{2+} ions. The detailed deconvolution of Co2$p_{3/2}$ region into components is presented in the paper.

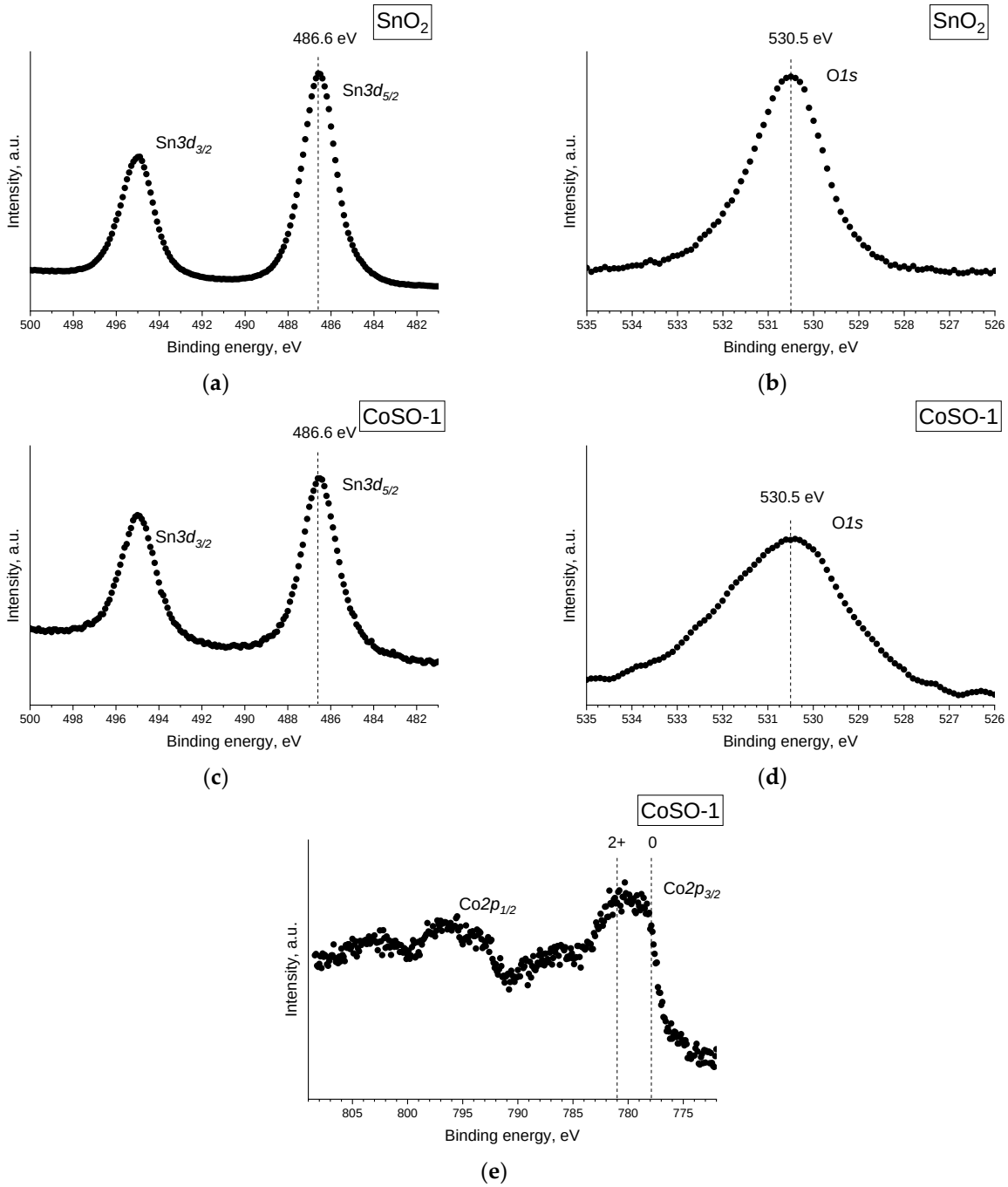


Figure S5. High resolution XPS spectra of Sn3*d* (**a, c**), O1*s* (**b, d**) and Co2*p* (**e**) in both as-prepared SnO_2 film (**a, b**) and SnO_2 film implanted with 40 keV Co^+ ions to the fluence of 1×10^{17} ions/cm^2 (**c, d, e**).

References

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