# Room temperature ferromagnetism in spin-coated anatase- and rutile-$Ti_{0.95}Fe_{0.05}O_2$ films

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**Abstract**

Thin films of $Ti_{1-x}Fe_xO_2$ ($x = 0$ and 0.05) have been prepared on sapphire substrates by the spin-on technique starting from metal–organic precursors. When heat treated in air at 550 and 700 °C respectively, these films present pure anatase and rutile structures as shown both by x-ray diffraction and Raman spectroscopy. Optical absorption indicates a high degree of transparency in the visible region. Such films show a very small magnetic moment at 300 K. However, when the anatase and the rutile films are annealed in a vacuum of $1 \times 10^{-5}$ Torr at 500 and 600 °C respectively, the magnetic moment, at 300 K, is strongly enhanced, reaching 0.46 $\mu_B$/Fe for the anatase sample and 0.48 $\mu_B$/Fe for the rutile one. The ferromagnetic Curie temperature of these samples is above 350 K. When the ferromagnetic rutile sample is reheated in air, the magnetic moment reduces strongly. The data seem to indicate that oxygen defects created as a result of vacuum annealing may be responsible for the observed ferromagnetism in our samples.

Transparent ferromagnetic semiconductors with ferromagnetic Curie temperature, $T_c > 300$ K, are expected to play a vital role in the development of spintronics [1]. Earlier reports based on III–V semiconductors such as GaAs, doped with Mn, revealed that $T_c$ hardly exceeded 150 K, rendering them unsuitable for viable room temperature applications [2]. Since then, the attention has turned towards the oxide semiconductors. Matsumoto *et al* [3] was the first to report the occurrence of ferromagnetism with $T_c > 300$ K in Co-doped $TiO_2$ films prepared by pulsed laser deposition (PLD). Following this, several reports have appeared on the occurrence of ferromagnetism above room temperature in other materials such as $TiO_2$ doped with Fe [4, 5], ZnO doped with Co [6, 7], GaN doped with Mn [8], AlN doped with Cr [9] and $SnO_2$ doped with Co [10] or with Fe [11]. The ferromagnetic samples examined were

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prepared using different preparative techniques such as oxygen-plasma-assisted molecular-beam epitaxy (MBE) [12], sputtering [13], ion implantation [14] and laser MBE [15] as well as PLD [5, 9, 10]. Though all these samples did show unambiguous signs of ferromagnetic behaviour at 300 K or above, it was difficult to exclude the possibility of formation of clusters of dopants and thus attribute the observed magnetism entirely to 3d element substituted in different hosts. Several arguments, for and against the formation of clusters, were proposed by these authors. It should be further noted that the double exchange mechanism [16], which is known to account for the ferromagnetism in mixed valence manganites, may not be applicable in the above materials. Another mechanism in vogue involves ferromagnetic coupling via spin-polarized p-band holes to account for the ferromagnetic behaviour in $Ga_{1-x}Mn_x As$ [17]. This model is also not expected to account for the ferromagnetic behaviour observed in the 3d doped oxides or nitrides. However, carrier-mediated ferromagnetism with $T_c > 300$ K has been predicted to occur in Mn-doped ZnO [18].

We have used a non-vacuum approach, known as the spin-on technique, to prepare Fe-substituted $TiO_2$ films. This is a well known technique that has been used to prepare $TiO_2$ films starting from metal–organic precursors [19]. Some of the salient features of this technique are low cost, simplicity, the possibility of using starting materials of high purity and the possibility of obtaining a homogeneous mixture of two cations in the liquid state. We report here on the successful preparation of 5% Fe-substituted $TiO_2$ films crystallizing either in anatase or rutile structure and present x-ray diffraction (XRD), optical absorption, Raman spectra and magnetization measurements. Though the as-prepared films showed a very weak ferromagnetic behaviour at 300 K, the vacuum-annealed films showed a strong enhancement in the magnetic moment of Fe.

The metal–organic precursors used were Ti–ethylhexoxide and Fe–ethylhexoxide. The solutions were thoroughly mixed in approximately 95 to 5 ratio (by volume) using an ultrasonic bath. A small amount of xylene was added to obtain the optimal viscosity needed for spin-coating. A few drops of this mixed solution were placed on a sapphire substrate (*c*-axis oriented, 25 $mm^2$ area) which was spun at 5000 rpm for 15 s. The sample was annealed in air at 550 °C for 1 min and the process was repeated five to ten times to build up the layer thickness. The thickness of the sample used in the present study was 500 nm. Several such samples were prepared and were subjected to different heat treatments in air. The EDX showed that the concentration of Fe was about 5%. Films were further vacuum annealed under $1 \times 10^{-5}$ Torr at 500 or 600 °C.

The as-prepared films with and without Fe heat treated at 550 °C in air show a pure anatase phase whereas the films annealed at 700 °C in air show a rutile structure, as revealed by XRD. For example, figures 1(a) and (b) show XRD patterns of undoped anatase- and rutile-$TiO_2$ films of ~1 $\mu$m thickness. The films are polycrystalline with no preferred orientation. The different phases of the films were further confirmed by Raman spectra as shown in figures 2(a) and 3(a), which clearly exhibit all the characteristic phonon modes expected for the two forms of $TiO_2$. These are in full agreement with the spectra observed in single-crystalline forms of anatase and rutile-$TiO_2$ both of which belong to the $D_{4h}$ space group [20, 21]. The broad band ~235 $cm^{-1}$ in rutile-$TiO_2$ (figure 3(a)) has been assigned as a combination line rather than a fundamental one-phonon process [21]. The mode at 144 $cm^{-1}$ ($B_{1g}$) is expected to be very weak in the pure rutile phase. The Raman spectra of $Ti_{0.95}Fe_{0.05}O_2$ (figures 2(b) and 3(b)) are identical to those of undoped $TiO_2$ films in respective forms, indicating that the structures are retained after doping with Fe. This suggests that the Fe dopants occupy the substitutional sites in the host lattice. Further, no noticeable changes in the spectra were seen due to the vacuum annealing (spectra not shown). The optical absorption spectra of anatase- and rutile-$Ti_{0.95}Fe_{0.05}O_2$ films with and without vacuum annealing are shown in figures 4 and 5. There are no drastic changes
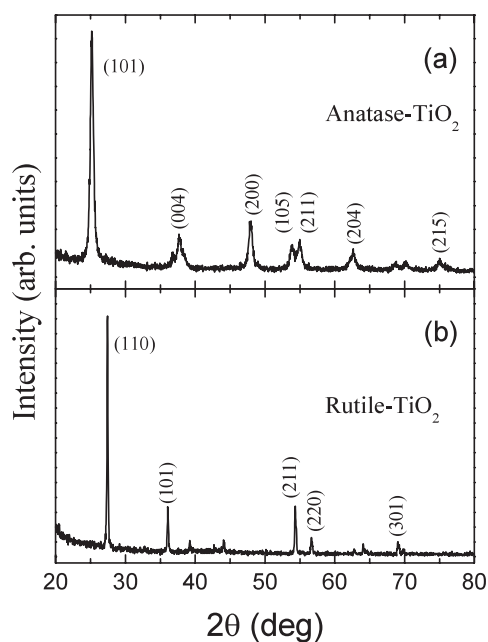
**Figure 1.** XRD $\theta$–$2\theta$ scans of (a) anatase and (b) rutile $TiO_2$ films.
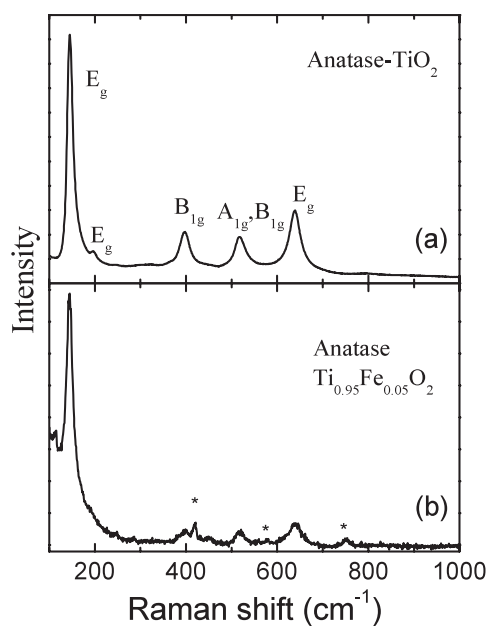


**Figure 2.** Raman spectra of anatase (a) $TiO_2$ and (b) $Ti_{0.95}Fe_{0.05}O_2$ films. The asterisks represent the peaks originating from the sapphire substrates.
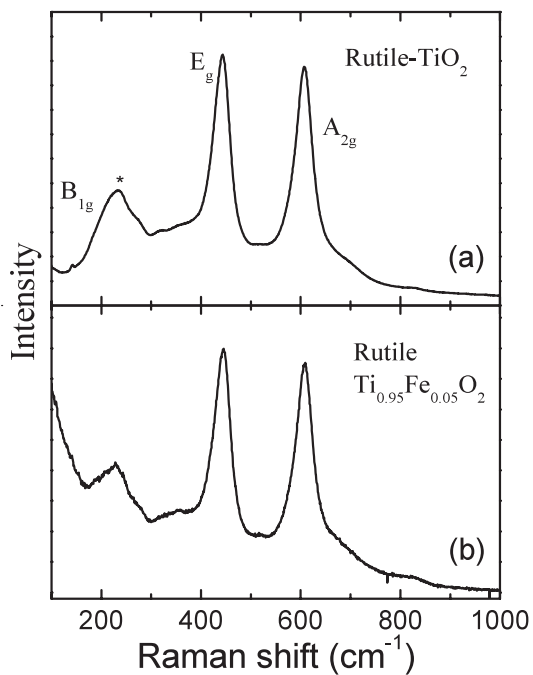


**Figure 3.** Raman spectra of rutile (a) $TiO_2$ and (b) $Ti_{0.95}Fe_{0.05}O_2$ films. The band marked with an asterisk is a combination band.

in the optical absorption spectra after vacuum annealing. The observed intensity oscillations, especially in the anatase film, in the wavelength region ($\lambda$) of 450–800 nm are due to thin film
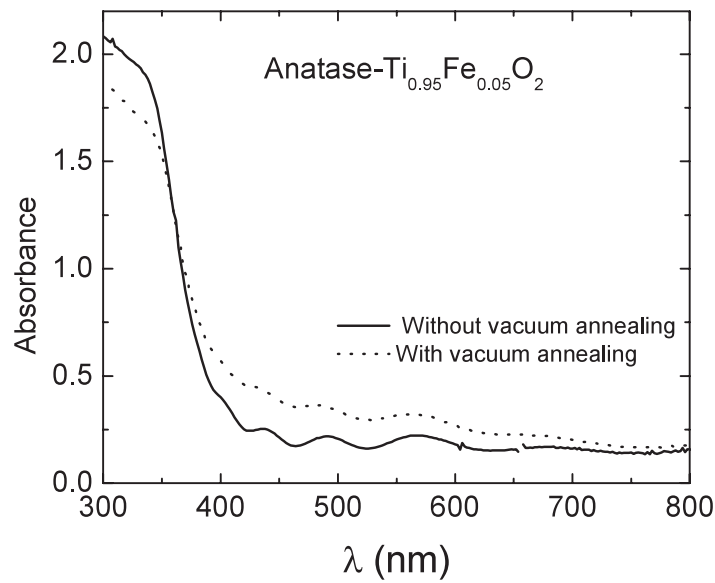
**Figure 4.** Optical absorption spectra of anatase-$Ti_{0.95}Fe_{0.05}O_2$ film before and after vacuum annealing.
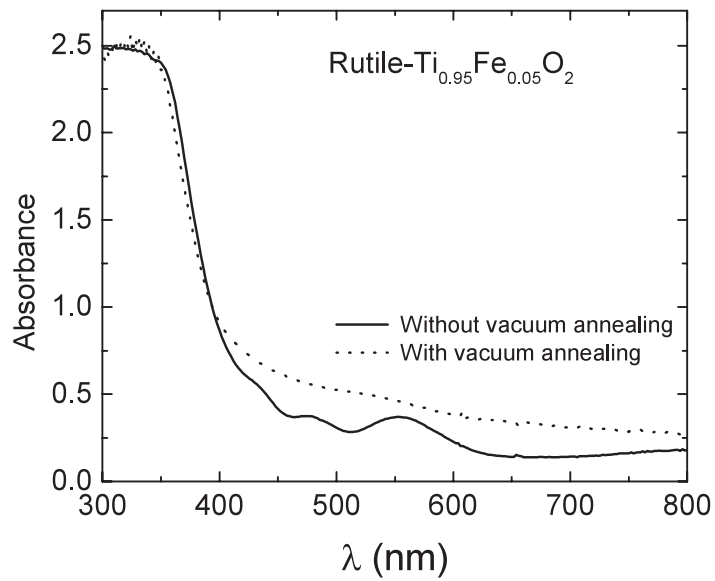


**Figure 5.** Optical absorption spectra of rutile-$Ti_{0.95}Fe_{0.05}O_2$ film before and after vacuum annealing.

optical interference effects, whereas the strong increase in the absorption for $\lambda < 400$ nm is due to electronic bandgap absorption. Anatase-$Ti_{0.95}Fe_{0.05}O_2$ has an absorption edge $\sim$350 nm, whereas the rutile-$Ti_{0.95}Fe_{0.05}O_2$ has an absorption edge at around 375 nm. These optical absorption edges are very close to the ones observed for undoped $TiO_2$ samples. The observed absorption edges in the present work are consistent with the reported values in the literature for the two forms of $TiO_2$.
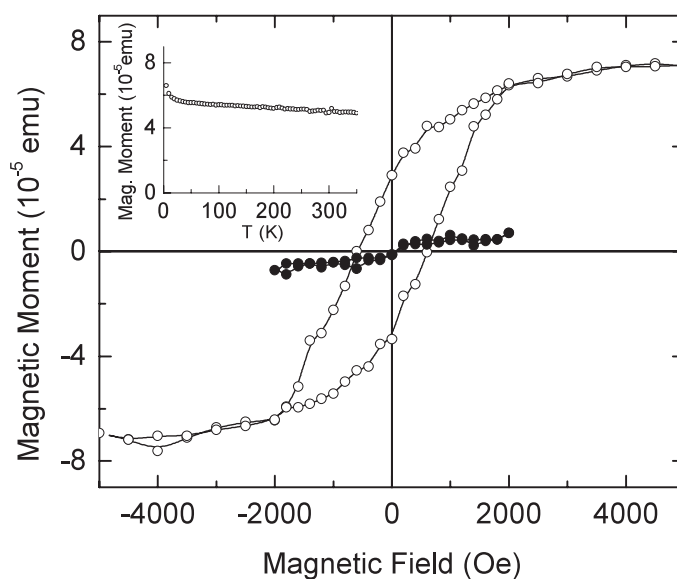
**Figure 6.** Magnetic moment at 300 K of the anatase-Ti$_{0.95}$Fe$_{0.05}$O$_2$ film as a function of magnetic field (symbols ● and ○ represent the data before and after vacuum annealing at 500 °C). The inset shows the magnetic moment versus temperature data in a field of 2000 Oe.

The magnetization ($M$) of the Fe substituted samples before and after vacuum annealing was measured as a function of temperature and magnetic field ($H$) using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. $M$ as a function of $H$ ($-5000$ to $5000$ Oe) at 300 K of the blank substrate was also measured in order to eliminate the substrate contribution. The data shown here thus represent the magnetization of the films. Figure 6 shows $M$ as a function of $H$ at 300 K of the anatase sample before and after annealing. Several interesting features can be noted. First, at 300 K, the as-prepared anatase form of the Fe substituted TiO$_2$ film shows a very small magnetic moment (0.03 $\mu_B$/Fe at 2000 Oe). Second, the vacuum annealed sample at 500 °C shows a strong enhancement in the ferromagnetic properties, the magnetic moment reaching a value of 0.46 $\mu_B$/Fe at 2000 Oe. Also, the coercivity increases remarkably from almost zero to 600 Oe as a result of this annealing. The remanent magnetization ($M_r$) at 300 K is 0.19 $\mu_B$/Fe. The magnetization of the rutile sample is also very sensitive to the vacuum annealing treatment but the behaviour is slightly different from that of the anatase sample (figure 7). The value of $M$ of the as-prepared rutile sample is ~0.09 $\mu_B$/Fe at 2000 Oe and increases to only 0.14 $\mu_B$/Fe after annealing at 500 °C. However, annealing the sample at 600 °C increases the magnetic moment to 0.48 $\mu_B$/Fe. A similar behaviour was observed in the Co-doped TiO$_2$ samples obtained by a similar spin-on technique [22]. The coercivity of the rutile sample also increases remarkably from a few Oe to 230 Oe. The value of $M_r$ is 0.12 $\mu_B$/Fe. Further, $M$ as a function of temperature, measured in a field of 2000 Oe, in the case of both the anatase and the rutile samples, after annealing at 500 and 600 °C respectively, is fairly constant from 5 to 350 K (figures 6 and 7 inset). Since the temperature range of our magnetization measurements is limited to 350 K, we expect our samples to remain ferromagnetic at least up to 400 K.

In what follows, we present a short discussion of our data in comparison with those published earlier and further comment briefly on a recent model that has been proposed by Coey *et al* [11] and Venkatesan *et al* [23] to account for the occurrence of ferromagnetism in
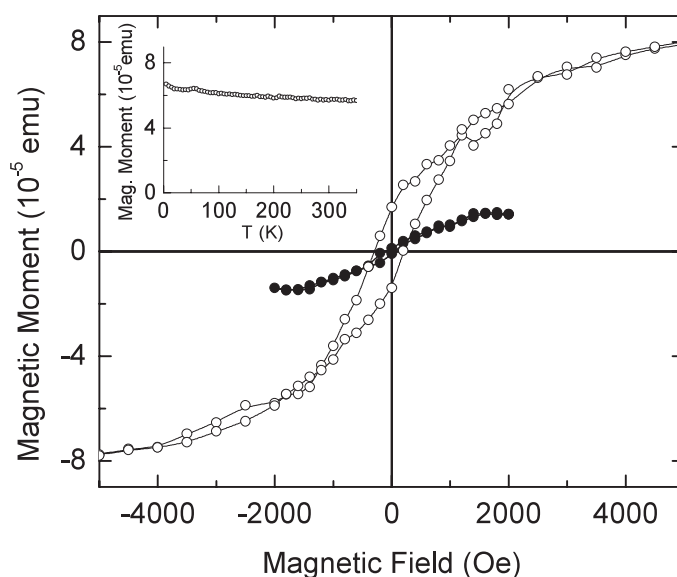
**Figure 7.** Magnetic moment at 300 K of the rutile-$Ti_{0.95}Fe_{0.05}O_2$ film as a function of magnetic field (symbols ● and ○ represent the data before and after vacuum annealing at 600 °C). The inset shows the corresponding magnetic moment versus temperature data in a field of 2000 Oe.

transparent semiconductors. To start with, we note that there have been very few reports on Fe-doped $TiO_2$. These describe either rutile phase [4, 24] or a mixture of anatase and rutile phase [25]. In contrast, we could obtain either the anatase phase or the rutile phase on the sapphire substrates just by selecting a proper heat treatment, as revealed unambiguously by Raman data. Further, the pure phases are retained after the heat treatment in vacuum. Next we comment on the magnetic moment of Fe obtained at 300 K. Wang *et al* [4] have reported a value of about 2.3 $\mu_B$/Fe in the case of 6% of Fe in $TiO_2$ whereas Hong *et al* [24] have obtained a value of 0.13 $\mu_B$/Fe in the case of 8% Fe-doped samples, though both these authors used the same method of pulsed laser ablation to prepare the doped films. Our values lie in between these values. The different values reported could be due to various factors. For example, some of the Fe can be present in the samples as clusters and some can be located at the Ti sites. Further, the presence of oxygen defects may also influence the magnetic moment. Indeed, in our case, the heat treatment has a remarkable effect on the value of $M$. The fact that the magnetic moment and the coercivity of the samples exhibiting anatase phase is different from that observed for the rutile phase samples may also indicate that the natures of oxygen defects are different in these two different phases. It is interesting to note that in the case of Co-doped ZnO films, the magnetic moment of Co strongly depended on the preparation conditions such as the partial pressure of oxygen, showing the role played by oxygen deficiencies [23]. Next, we comment on the formation of magnetic clusters in these films. Murakami *et al* [15] concluded from the EXAFS, XANES and XPS studies that their rutile films contained both Co metallic clusters and Co substituted into Ti site. Such studies have not been carried out on Fe-doped samples. We may note, however, that magnetic force microscope studies carried out in the case of Fe-doped $SnO_2$ samples [11] and V-doped $TiO_2$ samples [26] do not seem to support the formation of nanometre-sized clusters on the surface and thus the observed magnetic properties were taken to represent intrinsic behaviour of the samples. Since there is no exchange mechanism which could account for the observed data at low doping levels, Coey *et al* [11] have proposed a
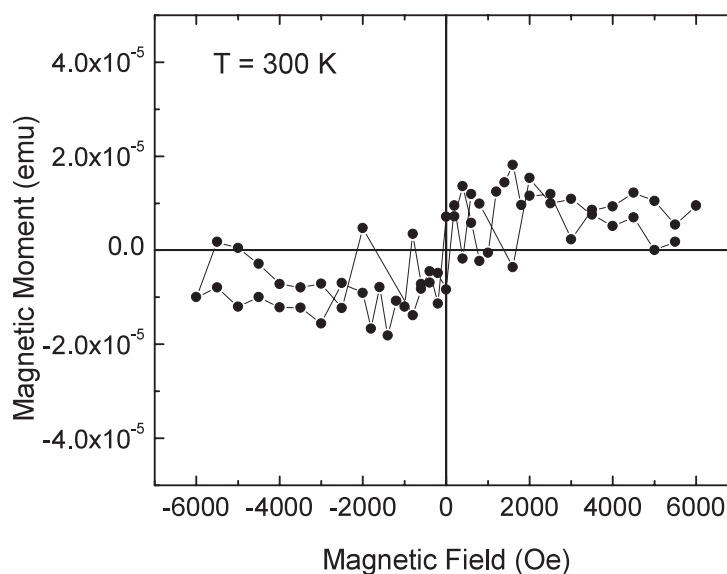
**Figure 8.** Magnetic moment at 300 K of the rutile-Ti$_{0.95}$Fe$_{0.05}$O$_2$ film as a function of magnetic field. Note that the film which had been vacuum annealed earlier was reheated in air at 700 °C before this measurement was carried out.

model where the exchange is mediated by carriers in a spin-split impurity band derived from extended donor orbitals. They point out that the oxygen vacancies play an important role. Though the details have not been worked out yet, this model is very appealing to us since annealing of our films in vacuum could possibly create oxygen vacancies that could influence the magnetic properties in this diluted system. To investigate if the oxygen vacancies do play a role in the appearance of ferromagnetism in our samples, one of the vacuum-annealed rutile-Ti$_{0.95}$Fe$_{0.05}$O$_2$ films which showed a clear ferromagnetic behaviour (figure 7) was reheated in air at 700 °C for 2 h and the magnetic moment was measured. Figure 8 shows the magnetic moment at 300 K of this reheated rutile-Ti$_{0.95}$Fe$_{0.05}$O$_2$ film as a function of magnetic field. Indeed the magnetic moment of this film was considerably reduced. The maximum value of the magnetic moment did not exceed 0.12 $\mu_B$/Fe which was much smaller than the saturation value obtained in the case of the vacuum-annealed sample. Further, one could hardly observe any coercivity. This seems to indicate the oxygen vacancies do play a major role in inducing ferromagnetism in these samples.

After the vacuum annealing, it may also induce another valence state of Ti, assuming Fe is in a valence state of 3. Detailed studies on the effect of annealing on the magnetic properties and the microstructure of the TiO$_2$ doped with Fe and other elements seem to be highly desirable in order to understand further this interesting aspect. Such studies are expected to throw further light on the role played by oxygen defects on the magnetic properties. We end this discussion by commenting on a recent theoretical work by Bergqvist *et al* [27]. By noting that the magnetic properties on oxide magnetic semiconductors depend very much on the preparation conditions, these authors propose a model based on magnetic percolation. They point out that the random distribution of magnetic atoms in the host lattice plays a crucial role and underline the importance of the localization of exchange interactions that have a strong directional dependence.

In summary, by using a low cost spin-on technique, we have successfully prepared Fe-($\approx$5%) substituted TiO$_2$ films on sapphire substrates both in the anatase and in the rutile

forms that show room temperature ferromagnetism. The magnetic properties are found to be enhanced as a result of annealing in vacuum. Upon annealing in vacuum at 500 °C, the magnetic moment and the coercivity, at 300 K, were found respectively to be 0.46 $\mu_B$/Fe and 600 Oe for the anatase sample and 0.48 $\mu_B$/Fe and 230 Oe for the rutile one. The magnetic moment of the rutile sample reduced considerably when reheated in air. Our data, though they cannot rule out the presence of Fe clusters, point out the important role played by oxygen defects in the ferromagnetic properties of Fe-substituted $TiO_2$ films.

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