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Author(s)	Nguyen, Hoa Hong; Prellier, W.; Sakai, Joe; Hassini, Awatef
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Description	

Fe- and Ni-doped TiO_2 thin films grown on $LaAlO_3$ and $SrTiO_3$ substrates by laser ablation

Nguyen Hoa Hong[a)]
Laboratoire LEMA, UMR 6157 CNRS/CEA, Université F. Rabelais, Parc de Grandmont, 37200 Tours, France

W. Prellier
Laboratoire CRISMAT, CNRS UMR 6508, ENSICAEN, 6 Bd Maréchal Juin, 14050 Caen, France

Joe Sakai
School of Materials Science, JAIST, Asahidai 1-1, Tatsunokuchi-machi, Ishikawa 923-1292, Japan

Awatef Hassini
Laboratoire LEMA, UMR 6157 CNRS/CEA, Université F. Rabelais, Parc de Grandmont, 37200 Tours, France

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Room temperature ferromagnetic Fe- and Ni-doped TiO_2 thin films were grown by the laser ablation on both $LaAlO_3$ and $SrTiO_3$ substrates. Most of the films are pure anatase, and only the films of Ni content of 3.6% and 4.6% are rutile. Films on $LaAlO_3$ substrates are more crystallized than films on $SrTiO_3$ substrates resulting from the lattice mismatch. Our magnetic measurements also suggest that the ferromagnetism in Fe/Ni:TiO_2 films is not due to Fe/Ni segregations but due to Fe/Ni:TiO_2 matrices. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1695103]

After the prediction of room temperature ferromagnetism (FM) for Mn-doped ZnO of Dietl *et al.*,[1] there has been a lot of research following this trend. According to theory,[2] doping V, Fe, Ni, Co, and Cr might introduce magnetism into a semiconducting oxide host. Since the discovery of Matsumoto *et al.*,[3] Co:TiO_2 thin films have attracted many research groups due to their exhibition of very high Curie temperature (T_C). While Co-doped ZnO or TiO_2 thin films have been fabricated by various techniques,[4–7] not much work has been done on Fe/Ni-doped ZnO or TiO_2 films. So far, no evidence of FM has been reported for Fe:ZnO films,[8,9] and for Ni:ZnO films, FM was found only at 2 K.[10] As regards to TiO_2 host, there have been very few reports on Fe and Ni dopings. Bally *et al.* found no FM in Fe:TiO_2 thin films,[11] while Wang *et al.* recently obtained high T_C ferromagnetic Fe:TiO_2 films only on sapphire substrates.[12] In this letter, we report about high T_C ferromagnetic Fe/Ni:TiO_2 thin films grown by laser ablation on both $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) substrates.

Fe/Ni:TiO_2 targets with the dopant concentration of 8% were synthesized by a sol-gel method. 2700-Å-thick-Fe/Ni:TiO_2 films were deposited by the pulsed laser deposition (PLD) technique (248 nm KrF excimer laser, pulses of 5 Hz) on (001) LAO and (001) STO substrates. The oxygen partial pressure (P_{O^2}) was 10^{-6} Torr, and the energy density was 1, 1.5, 3, or 5 J/cm^2. The substrate temperature was 700 °C. After deposition, all films were cooled down to room temperature under a P_{O^2} of 20 mTorr.

Fe-doped films are pink and Ni-doped films are transparent, and they are very shiny indicating very smooth surfaces. From the RBS data, the Fe content was estimated to be 8.1% and 12.6% for the films grown under the fluence of 1.5 and 3 J/cm^2, while the Ni content was 3.6%, 4.3%, 4.6%, and 5.2% for the films grown under the fluence of 1, 1.5, 3, and 5 J/cm^2, respectively.

XRD showed that all of our films are well epitaxial (from Φ scan not shown) and highly *c*-axis oriented. While only Ni:TiO_2 films of Ni=3.6% and 4.6% deposited on LAO show rutile structure [Fig. 3(c)], all other Fe/Ni:TiO_2 films grown on both types of substrates are single phased anatase [Figs. 1, 2(a), and 2(b)]. We did not see any trace of impurities, at least from the XRD data. The diffraction peaks which are more intense and sharper for films on LAO than those of films on STO indicate a better crystallinity on LAO. As observed previously, this is a result of the smaller lattice

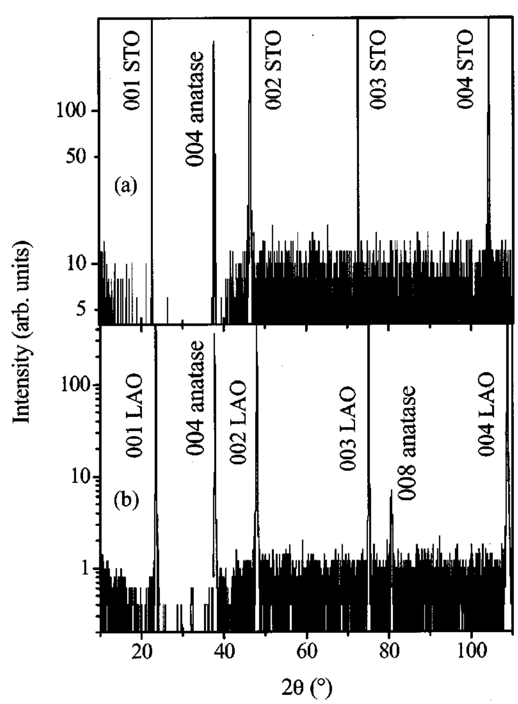

FIG. 1. XRD for a $Ti_{0.919}Fe_{0.081}O_2$ film deposited on (a) STO and (b) LAO.

[a)]Electronic mail: hoahong@delphi.phys.univ-tours.fr

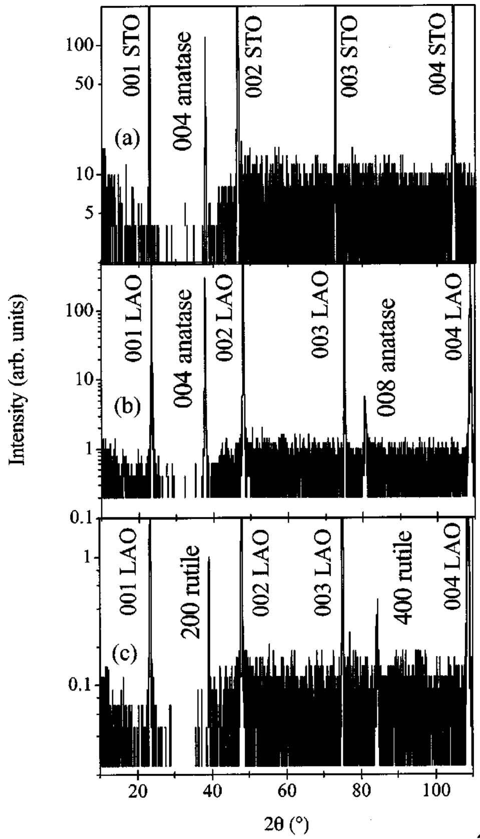

FIG. 2. XRD for $NiTiO_2$ films: (a) $Ti_{0.957}Ni_{0.043}O_2$/STO, (b) $Ti_{0.957}Ni_{0.043}O_2$/LAO, and (c) $Ti_{0.954}Ni_{0.046}O_2$/LAO Note that for $Ti_{0.954}Ni_{0.046}O_2$, the film exhibits a rutile structure.

mismatch.[13] By comparing Fig. 2(a) and Fig. 2(b), Fig. 3(a) and Fig. 3(b), we can see that the 008 anatase diffraction peak (at $2\theta=80°$), which was observed in films on LAO, is not clearly seen in films on STO. This might be due to a difference in oxygen vacancies which may vary from one substrate to another. At some critical point, it might be claimed to the formation of Magnéli shear planes.[12] However, the formation of that plane is more common in the case of rutile TiO_2 crystallizing in a tetragonal lattice, but the films that we are discussing are anatase. Thus, it seems that the lack of that peak is more reasonable to be caused by oxygen. The out-of-plane lattice parameters of films with various contents of Fe/Ni on STO/LAO are summarized in Table I. One can see that for STO substrates, the lattice parameter basically increases upon Fe doping (compared to the nondoped TiO_2 parameter as of 9.513 Å),[14] but above 8.1% it remains almost constant versus Fe content, while the lattice parameter increases upon Ni doping as Ni content is up to 4.3%, and then decreases a bit. This suggested that Fe/Ni was really substituted for Ti in TiO_2 and the doping does not deteriorate the anatase structure. On LAO substrates, the situation is more complicated. While in the Fe doping case, the lattice parameter does not change much versus the Fe content and the structure remains thoroughly as anatase, in the Ni doping case, as the Ni content is 3.6% or 4.6% [Fig. 2(c)], the films were crystallized in a rutile-type structure with a c-axis length of 4.597 or 4.588 Å (in comparison to 4.595 Å of nondoped TiO_2 rutile).[15] So far, no rutile Co/Fe/Ni:TiO_2 thin film has been obtained on either LAO or STO substrates. This case is rare and interesting, since this

TABLE I. Evolution of the out-of-plane lattice parameters for various films with different contents of Fe and Ni on two types of substrates. Diffraction peaks correspond to an anatase-type phase except for the films of 4.6% and 5.13% of Ni on LAO (marked by an asterisk) where the films crystallized in a rutile-type structure (anatase TiO_2 has $c=9.513$ Å and rutile has $a=4.595$ Å).

		Substrate	
Dopant	Content	$SrTiO_3$ (Å)	$LaAlO_3$
Fe	8.1%	9.532	9.512 Å
	12.6%	9.536	9.516 Å
	3.6%	9.531	4.597 Å (*)
Ni	4.3%	9.536	9.516 Å
	4.6%	9.512	4.588 Å (*)
	5.2%	9.522	9.512 Å

phase is very thermodynamically stable at high temperatures. Reference 11 reported that the doping might induce a structural transition from anatase to rutile above some critical dopant concentration. However, in our case, because all films with various Ni contents on STO are anatase, and the films of Ni=4.3% and 5.2% grown on LAO are anatase as well, even though the films of Ni=3.6% and 4.6% on LAO are rutile, it is not likely that there is any critical point for a structural transition. The assumption in a recent study on Er:TiO_2 films which suggested that the P_{O^2} during deposition would define a doped TiO_2 films to be anatase or rutile[16] also cannot explain our case, since all films were deposited under the same P_{O^2}. By comparing the out-of-plane lattice parameters of the films grown on LAO or STO, we also found that the c-axis lattice parameters are smaller for films on LAO compared to those on STO (for the same dopant content). This is quite opposite to the previous reports about substrate effects in oxide thin films[17] therefore, it implies the presence of oxygen vacancies in our films.

The $M(T)$ curves taken at 0.2 T for Fe:TiO_2 films are shown in Fig. 3(a). Except for the film of Fe=12.6% on STO which shows a weak FM below 50 K, and a superparamagnetism for higher temperatures, all other films are ferromagnetic with T_C higher than 400 K. Figure 3(b) shows the $M(H)$ curve taken at 300 K for the film of Fe=8.1% on LAO. The observed hysteresis loop shows that the film is ferromagnetic at room temperature. In fact, a large saturation magnetization (M_s) was expected to obtain in Fe:TiO_2 films but the maximum M_s in our films is found to be only 0.14 μ_B per Fe atom. While only the film of Ni=4.3% is superparamagnetic, all other films on LAO are room temperature ferromagnetic with the M_s being 2.7, 0.3, and 1.3 μ_B for Ni=3.6%, 4.6%, and 5.2%, respectively. As seen in Fig. 4(a), the magnetization starts to fall near 400 K, therefore, the T_C is estimated to be just a bit higher. From the magnetization data in Fig. 4 and parameters shown in Table I, one can see that the films of Ni content of 3.6% and 5.2% on LAO whose parameters are closest to the nondoped TiO_2 parameters (rutile and anatase) have the largest M_s [referring Fig. 4(a)]. It seems that in these cases, Ni was well substituted for Ti in the TiO_2 host, and we obtained a solid solution. By contrast, Ni:TiO_2/STO films showed a weaker FM, either with a smaller M_s (as Ni=3.6% and 5.2%) or low T_C (as Ni=4.3% and 4.6%) [Fig. 4(b)].

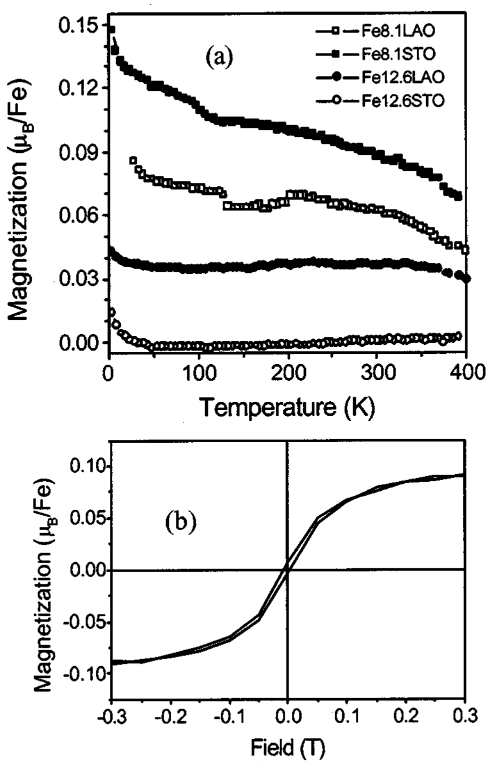

FIG. 3. Magnetization of Fe:TiO_2 films (a) vs temperature at 0.2 T for various Fe contents on both substrates and (b) vs magnetic field at 300 K for the film of Fe=8.1% on LAO. In each case, a bare substrate with the same size as of the film ($0.5\ cm \times 0.5\ cm$) was measured at the same field or temperature in order to subtract directly.

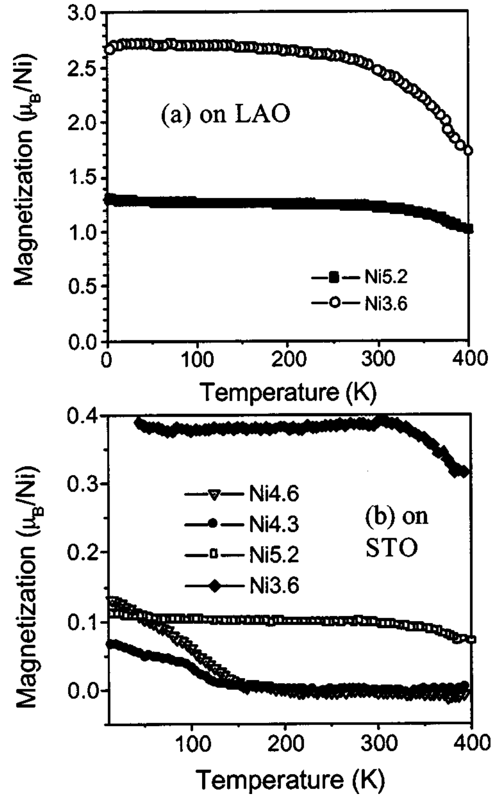

FIG. 4. Magnetization vs temperature at 0.2 T for (a) Ni:TiO_2 films with Ni content of 3.6% and 5.2% on LAO and (b) Ni:TiO_2 films with various Ni contents on STO.

Among all of the transition metal-doped TiO_2 films on LAO we have made, Ni-doped films have the largest M_s (larger than that of Fe-doped films mentioned earlier and also larger than M_s of Co:TiO_2 films which were fabricated under the same condition[7]). This is unexpected because Ni metal has the lowest T_C and the smallest M_s among Fe, Co, and Ni, as regards to magnetism of each individual element. This is an additional indirect evidence to show that the FM does not come from Fe/Ni metal or clusters, but from the Fe/Ni:TiO_2 matrices, besides the fact that our Fe/Ni-doped films do not have the T_C as high as 1043 K (if it is from Fe metal) or 627 K (if it is from Ni metal). Note that in our films, FM is not caused by Fe or Ni particles because if it happened, M_s must be 2.22 μ_B for the Fe case and 0.6 μ_B for Ni case, but the M_s of our films is much smaller in Fe case (as 0.14 μ_B/Fe) and much larger in Ni case (as 2.7 μ_B). The XRD pictures which show no trace of Fe and Ni metal as well as of iron and nickel oxides, along with the smooth surface observed by SEM, likely rule out the possibility of having Fe/Ni clusters.

We obtained pure anatase Fe:TiO_2 films and anatase or rutile Ni:TiO_2 films grown on both LAO and STO substrates. While most of Fe:TiO_2 films show FM above room temperature with a rather modest M_s, the only Ni:TiO_2 films on LAO whose lattice parameters are closest to that of non-doped TiO_2 are strongly ferromagnetic with a large M_s. The pure rutile structure in films grown on LAO is rather special, because so far, transition metal-doped TiO_2 films on either STO or LAO substrates are often anatase. All films are single phase and highly crystallized. Due to the smaller lattice mismatch in the case of LAO, films on LAO are more oriented and crystallized than films on STO.

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