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Magnetism in Ni-doped SnO_2 thin films

Nguyen Hoa Hong[1,4], Antoine Ruyter[1], W Prellier[2], Joe Sakai[3] and Ngo Thu Huong[3]

[1] Laboratoire LEMA, UMR 6157 CNRS-CEA, Université F Rabelais, Parc de Grandmont, 37200 Tours, France
[2] Laboratoire CRISMAT, UMR 6508 CNRS, ENSICAEN, 6 Bd du Maréchal Juin 14050 Caen, France
[3] School of Materials Science, JAIST, Asahidai 1-1, Nomi Ishikawa 923-1292, Japan

E-mail: hoahong@delphi.phys.univ-tours.fr and nguyen.hoahong@univ-tours.fr

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Abstract

Transparent Ni-doped SnO_2 thin films grown by the pulsed laser deposition technique on $LaAlO_3$, $SrTiO_3$ as well as R-cut Al_2O_3 substrates all show room-temperature ferromagnetism (FM). While the Ni-doped SnO_2 films on $LaAlO_3$ substrates have a large magnetic moment of about 2 μ_B/Ni, films grown under the same conditions on $SrTiO_3$ and Al_2O_3 substrates have a magnetic moment of one order smaller. Magnetic force microscopy measurements confirmed that the Ni:SnO_2 films on $LaAlO_3$ are magnetically homogeneous at nanometre-scales, and the FM in the films comes from the doped matrix.

(Some figures in this article are in colour only in the electronic version)

Over the last few years, doping a transition metal (TM) in semiconducting oxides in order to induce room-temperature ferromagnetism (FM) has become one of interesting topics for many physics groups. Many results have been reported for Co/Fe/Ni/V/Cr-doped TiO_2 or ZnO [1–4], but there is still little work on TM-doped SnO_2. While Mn doping in SnO_2 does not result in FM [5], Co:SnO_2, Fe:SnO_2, Cr:SnO_2 and V:SnO_2 films show strong FM at very high temperatures [6–9]. In this paper, we report on the magnetism of Ni-doped SnO_2 thin films deposited on different types of substrates.

Ni:SnO_2 films with a typical thickness of 220 nm were grown on (001) $LaAlO_3$ (LAO), (001) $SrTiO_3$ (STO) and R-cut Al_2O_3 substrates by using the pulsed laser deposition (PLD) technique (KrF laser with $\lambda = 248$ nm) from a $Sn_{0.95}Ni_{0.05}O_2$ ceramic target. The repetition rate was 10 Hz and the energy density was 1.8 J cm^{-2}. The substrate temperature was 700 °C. During deposition, the oxygen partial pressure (P_{O2}) was kept as 10^{-4} Torr, and after deposition, the films were cooled down slowly to room temperature under the same

[4] Author to whom any correspondence should be addressed.

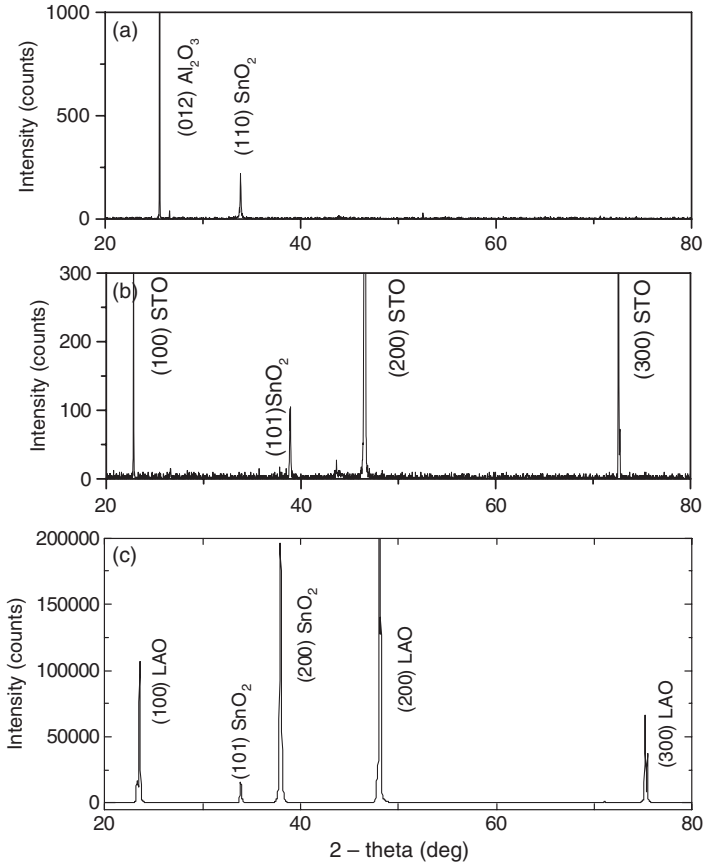

Figure 1. XRD data in linear scale for Ni:SnO_2 films (a) on Al_2O_3; (b) on STO; and (c) on LAO substrates.

oxygen pressure as during deposition. The structural study was done by x-ray diffraction (XRD) using a Seifert XRD 3000P. The magnetic measurements were performed by using a Quantum Design superconducting quantum interference device (SQUID) system from 0 up to 0.5 T under a range of temperatures from 400 K down to 5 K and a magnetic force microscope (NT-MDT) operated at room temperature in zero field. The composition was checked by using Rutherford backscattering (RBS) microscope.

The Ni content in the films was determined by RBS data to be 8.33% (note that the relative error of RBS is 4%). In spite of the difference in substrates, all Ni:SnO_2 films are highly transparent. XRD data showed that the films on three types of substrates are basically formed as SnO_2 structure. As for films on STO substrates, the diffraction patterns show that the (101) peak of SnO_2 is most apparent, while for films on Al_2O_3 substrates, the most revealing peak is (110). In the case of films on LAO substrates, besides the (101) orientation that is similar to that of films on STO, the (200) peak of SnO_2 also appears strongly, and the films seem to have a much better crystallinity. (Peaks of films on LAO shown in figure 1(c) have much larger intensities compared to those shown in figures 1(a) and (b) for films on Al_2O_3 and STO (four orders larger). Also, the spectra of films on LAO show no peak of any secondary phase, while in those of films on Al_2O_3 and STO, some small peaks of another phase exist.) As regards the films on STO and Al_2O_3, the out-of-plane parameters are 2.31 and 2.64 Å,

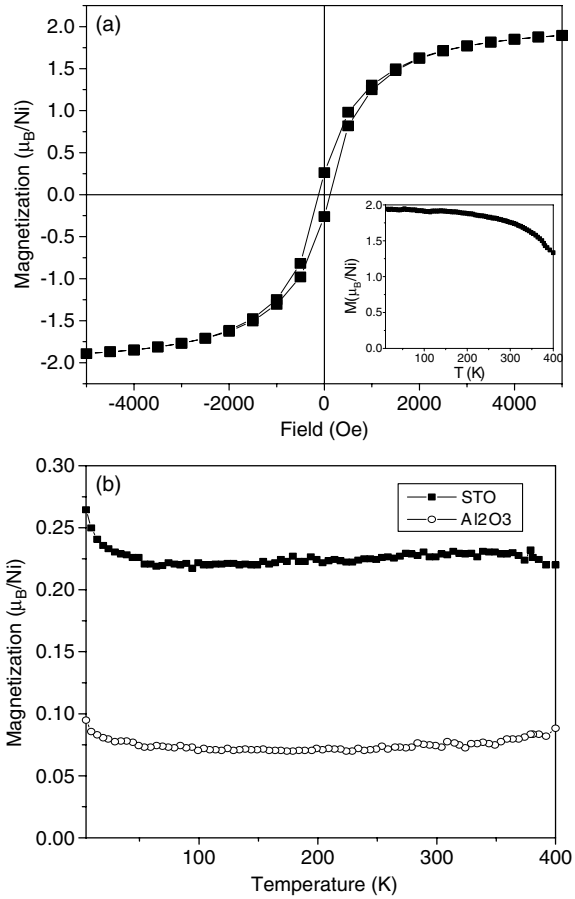

Figure 2. (a) Magnetization versus magnetic field taken at 300 K for a Ni:SnO_2 film on LAO substrate. The inset shows the M–T curve taken at 0.5 T. (b) Magnetization versus temperature taken at 0.5 T for Ni:SnO_2 film on STO and Al_2O_3 substrates.

respectively. Those parameters are almost the same as those of Cr-doped SnO_2 films with the same dopant concentration and the same growth conditions [8], but quite different from those of bulk SnO_2 (tetragonal: $a = 4.738$ Å and $c = 3.187$ Å) [10]. In the case of films on LAO, the lattice parameters were found very close to those of the bulk (tetragonal: $a = 4.744$ Å and $c = 3.1891$ Å), and perhaps in this case, Ni was really substituted for Sn in SnO_2 which might result in a solid solution.

The magnetization versus magnetic field taken at 300 K for the Ni:SnO_2 film on LAO is shown in figure 2(a). A very well defined hysteresis loop was observed, showing that the film is certainly ferromagnetic at room temperature (note that there is surely no contamination of the substrate, since the magnetization measurements for bare LAO substrates all strongly confirmed that they are clearly diamagnetic). The saturated magnetization (M_s) in this case is almost 2 μ_B/Ni if one supposes that all the Ni atoms in the film contribute to its magnetism. From the inset of figure 2 for the M–T curve taken at 0.5 T, one can see that the sample has T_C beyond 400 K, and the curve remains almost monotonic for the whole range of temperatures below T_C. This is indirect evidence for having no clusters in this film, because according to [11], M–T curves for samples with magnetic clusters must have some anomaly at low

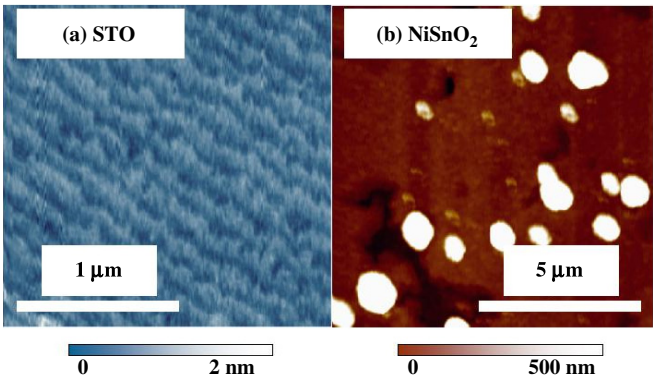

Figure 3. Topography images recorded on an area of 2 μm × 2 μm for an STO substrate (a) and on an area of 10 μm × 10 μm of the Ni:SnO_2 film on STO (b).

temperatures. The value of M_s of 2 μ_B/Ni and T_C around 400 K could not come from Ni metal clusters, because Ni metal has M_s of 0.6 μ_B/Ni along with T_C of 627 K [12]. Thus, the large magnetic moment obtained in Ni:SnO_2 films on LAO is more likely intrinsic.

Compared to Ni:SnO_2 films on LAO, Ni:SnO_2 films grown under the same fabrication conditions on STO and Al_2O_3 substrates have a much smaller magnetic moment (note that three different substrates were fixed simultaneously in one run). Even though films on those two types of substrates are definitely FM above room temperature (see figure 2(b) for M–T curves taken at 0.5 T showing T_C higher than 400 K), the magnitude of the magnetic moment is much smaller than that of films on LAO. M_s is about 0.2 μ_B/Ni and 0.1 μ_B/Ni for films on STO and Al_2O_3, respectively. These values are almost as large as those of Co:TiO_2 films on STO [13]. The tendency of M–T curves to increase at very low temperatures (below 30 K) suggests that in the films on STO and Al_2O_3, there might be the possibility for some antiferromagnetic precipitations to exist [11], and those might not be detected by XRD due to a detection limit of less than 5%. Their contributions could be the reason for a reduction of the magnitude of the magnetic moment in these two cases. One explanation for the large difference in magnetic moment of films on LAO and films on STO and Al_2O_3 is that it may be due to the difference in lattice parameters for films on different substrates: in the case of films on LAO, the films are better crystallized, and a solid solution could be achieved; therefore, as a consequence, this could result in a much larger magnetic moment (very similar to the case of Ni:TiO_2 films on LAO: the films whose parameters are closest to the non-doped parameters have the largest magnetic moment) [14]. Another reason might be due to a big discrepancy in morphology of different substrates. From the topography images, we observed a big difference in the surface morphology of LAO and STO substrates, which might somehow explain the issue. From figure 3(a), one can see that STO substrate is very rough. (The roughness is about 0.13 nm; but it is periodic with steps. Taking the roughness is taking the average only, and the averaging masks any really big difference. The distance from peak to peak should be seen clearly.) In contrast, the LAO substrate has a very smooth and flat surface (from figure 4(a) the roughness could be determined as about 0.09 nm; but note that apart from some very high peaks, the overall substrate is quite flat). The rough surface of STO (and similarly, Al_2O_3), must be the reason for the modification of the morphology of the deposited films, as well as the structural nature of the compounds at the interface, so that some precipitations could be formed more easily when we deposited films on STO (as well as Al_2O_3), in comparison with films grown on LAO. Therefore, it might cause such a reduction in the magnetic moments. From another

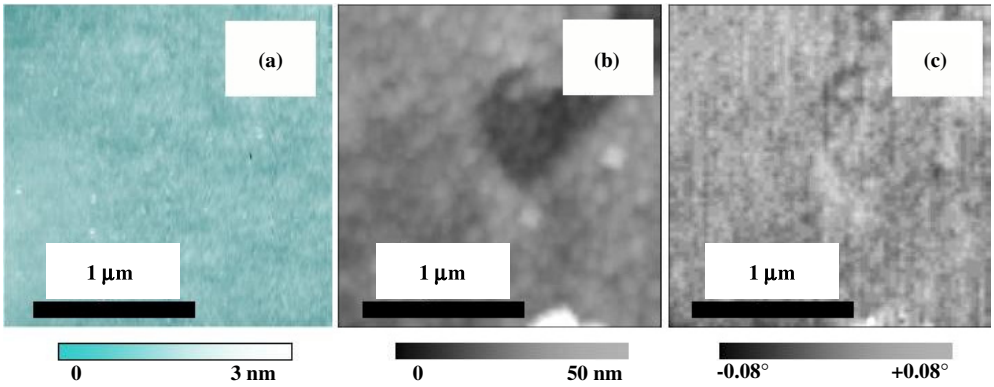

Figure 4. Topography images recorded on an area of 2 μm × 2 μm for an LAO substrate (a), for an Ni:SnO_2 film on LAO (b) and the corresponding MFM image (c). Note that the tip was magnetized perpendicular to the film plane.

viewpoint, one always can say that there is a difference in dielectric constants of the films and the substrates, so that for different substrates, there must be some induced different polarization effects and electric gradient in the films that may contribute somewhat to the difference in the resulting magnetism. For the Ni:SnO_2 film on STO, topography measurements on a small scale showed that there are many large parts of outgrowth that could be antiferromagnetic precipitations (figure 3(b)).

To confirm the room-temperature FM of the films, as well as to examine their magnetic homogeneity, magnetic force microscopy (MFM) measurements were performed at room temperature. (At first, the topography image was taken by using a non-contact mode. Then, the cantilever was lifted to a suitable height for each scan line after the topography measurement. Thus, the cantilever resonance oscillations can be used to detect the magnetic force signals, which are proportional to the second derivative of the stray field.)

For Ni:SnO_2 on STO and Al_2O_3 substrates, due to those very big particles on the surface, when taking the MFM images, on lifting the tip in order to eliminate the van der Waals forces, the distance between the magnetized tip and the film surface becomes larger than the distance over which the magnetic signals could still be detected; therefore, the MFM measurements could not be performed.

Figures 4(b) and (c) show a typical example for a topography image and a corresponding MFM image of an Ni:SnO_2 film on LAO. One can see that the contrasts on the MFM image (figure 4(c)) do not match the ones on the topography image (figure 4(b)), so that the magnetic signal certainly is not due to any surface effect but to the real magnetic signal of the sample. The recorded signal confirmed the FM at room temperature of the film. Moreover, in this scale, no clear contrast was observed on the MFM image, and the film shows a magnetic phase shift, which is almost constant ($\Delta\varphi = 0.16°$) for the whole specimen, reflecting a magnetically good homogeneity at nanometre-scale in the film with no trace of any clusters. On comparing with standard pictures of films with magnetic dots or clusters (which showed much clearer contrasts), this MFM image is completely different, and this suggests that the magnetism is in-plane for Ni:SnO_2 films [15, 16]. We also tried to perform the measurements on large scales of 20 μm × 20 μm in order to determine the size of the ferromagnetic domains, but there was no success since it was impossible to avoid touching parts that had a large height over a rather wide region. And if the tip was lifted too far way from the peaks, then the consequence was that it would become too far away to be able to detect any signal.

In conclusion, Ni-doped SnO_2 thin films grown on three types of substrates all are room-temperature ferromagnetic. Films grown on LAO substrates have a large magnetic moment of about 2 μ_B/Ni, about one order larger than that of films grown under the same conditions on STO and Al_2O_3 substrates. It is assumed that in the case of STO and Al_2O_3 substrates, there might be some antiferromagnetic precipitations of nickel oxide that probably contribute to the magnetism of those films, and as a consequence, the FM is reduced. As regards the Ni:SnO_2 films on LAO substrates, the large magnetic moment likely originates from the doped matrix. The MFM measurement confirmed their magnetic homogeneity.

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