Extrinsic origin of ferromagnetism in single crystalline $LaAlO_3$ substrates and oxide films

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Commercial $LaAlO_3$ substrates were thermally cycled simulating a procedure similar to those followed during TiO_2 and SnO_2 dilute magnetic semiconductors' film pulsed laser deposition. Ferromagneticlike behavior was found in some substrates, in which metallic iron impurities were detected by x-ray photoelectron spectroscopy and total reflection x-ray fluorescence measurements. A thorough experimental investigation, using high resolution techniques, showed that these impurities were introduced by the procedure used to fix the substrates to the oven silicon holders. It is suggested that magnetism observed previously in nominally pure SnO_2 films is of extrinsic origin. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2952839]

Interesting results have been reported showing room temperature ferromagnetism in pure TiO_2, HfO_2, In_2O_3, and SnO_2 oxide films.[1–4] The observed saturation magnetization was in all cases of the order of 20–30 emu/cm^3 and the magnetic moment (in films deposited on $LaAlO_3$ with a surface of 0.5×0.5 cm^2) of the order of $(1-15)\times10^{-5}$ emu. In these works it was concluded that defects, especially oxygen vacancies, could be the reason of the observed magnetism.

However, the appearance of magnetism in nominally pure oxide films continues to be a controversial issue which requires additional and careful experimental work. Some researchers have argued that ferromagnetism may originate from impurities already present in the commercially available substrates,[5,6] imparted to the substrates when these are handled with stainless-steel tweezers,[7] or transferred to them from external pollution.[8]

We have observed ferromagneticlike behavior in TiO_2 (Ref. 9) and SnO_2 (Ref. 10) pure films, deposited by pulsed laser deposition on $LaAlO_3$ substrates. The recorded saturation magnetization was of the order of those reported in Refs. 1–4. In Fig. 1, we show a plot where our pure films' magnetic moments are compared with those reported in literature. It can be observed that coercivity (a few tens of Oersteds) and saturation fields (0.2–0.3 T) are also of the order of those reported in literature for pure oxide films. In our case, samples were handled with plastic tweezers and the absence of ferromagnetism in the used ablation targets, magnetic measurement sample holders (straws), and $LaAlO_3$ as received substrates was checked.

In order to bring more insight to this problem we present an experimental study which demonstrates the existence of another possible source of contamination and magnetism related to the ablation chamber sample-mounting procedure.

Five $LaAlO_3$ (LAO) substrates were subsequently mounted onto a heater block and thermally cycled simulating a procedure similar to those followed during real film deposition. All of them were treated under nominally identical conditions, but ferromagneticlike behavior was found in just three of these substrates. In order to check for contaminating impurities, x-ray photoelectron spectroscopy (XPS) and total reflection x-ray fluorescence (TXRF) measurements were performed. We found a correlation between iron impurities and ferromagnetic behavior.

Figure 2 shows M versus H curves obtained from LAO (as received commercial single crystalline $LaAlO_3$) and LAOTTs (thermally treated LAOs). The thermal treatments were performed at 650 °C for 20 min in a reduced oxygen pressure of 4 Pa (TT1, 2, 3, 4, and 5) inside the laser ablation chamber. The magnetic measurements were performed with a commercial superconducting quantum interferometer device.

It can be seen that while LAO and LAOTT2 and 3 are completely diamagnetic, LAOTT1, 4, and 5 loops display the

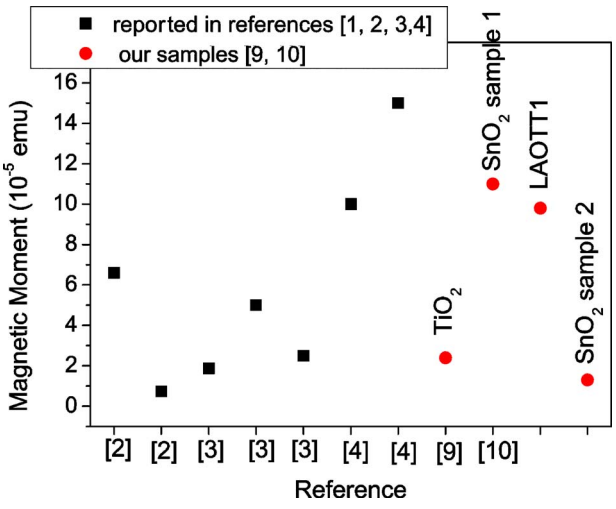

FIG. 1. (Color online) Reported magnetic moments of nominally pure oxide films.

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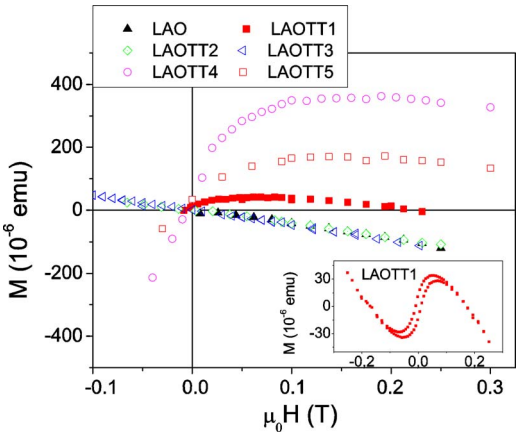

FIG. 2. (Color online) Magnetic moment vs magnetic field at 300 K for LAO and LAOTT1–5. The inset shows the complete hysteresis loop for LAOTT1.

superposition of diamagnetic and ferromagneticlike patterns. After the subtraction of the diamagnetic contribution the remaining component has a magnetic moment at saturations of 0.9, 4.6, and 2.7×10^{-4} emu for LAOTT1, 4, and 5, respectively.

Figures 3(a) and 3(b) show field cooling and zero field cooling $M(T)$ curves of LAO and LAOTT1 taken under 0.05 and 1 T applied field. As can be seen, in both materials a paramagnetic contribution can be distinguished. In order to separate the ferromagneticlike contribution observed in LAOTT1 from the diamagnetic and paramagnetic ones present in the LAO, the $M(T)$ curves of LAO were subtracted from LAOTT1 ones; the results are shown in Fig. 2(c). It can be seen that the difference between LAOTT1 and LAO does not show the paramagnetic contribution, indicating that atoms which contribute paramagnetically in LAO remain paramagnetic after the thermal treatment. On the other hand, the rather flat $M(T)$ shape of the remaining contribution suggests that the ferromagneticlike component has a Curie temperature considerably higher than 300 K.

As the furnace is located in the vertical position within the chamber the substrates were fixed to a silicon substrate with Ag paint. Two different commercial paints were used: A and B. LAOTT2 and 3 were fixed with paint A and

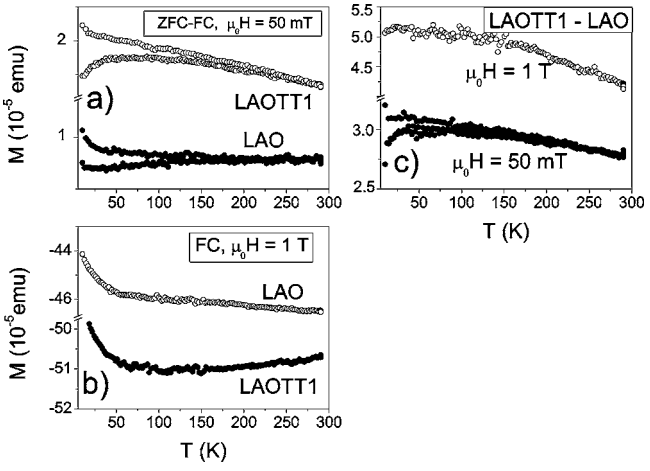

FIG. 3. LAO and LAOTT1 field cooling and zero field cooling magnetization vs temperature at (a) 0.05 T and (b) 1 T applied fields. (c) $M(T)$ curves after the subtraction of LAO from LAOTT1 ones.

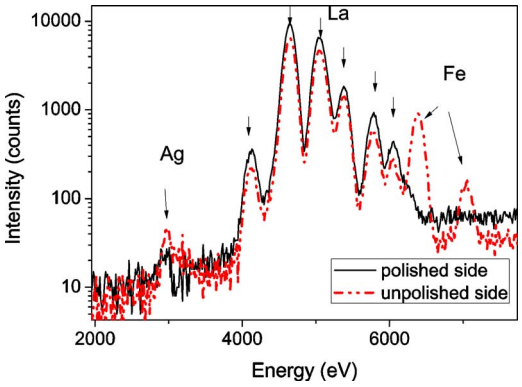

FIG. 4. (Color online) Synchrotron radiation TXRF spectra of polished and unpolished surfaces of LAOTT1 substrate.

LAOTT1, 4, and 5 with paint B. This fact was the only difference in the thermal treatment procedure, pointing to the Ag paint B as the possible source of contamination capable of inducing the observed ferromagneticlike behavior.

In order to check for impurities contamination XPS measurements were performed using a Mg $K\alpha$ source (XR50, Specs GmbH) and a hemispherical electron energy analyzer (PHOIBOS 100, Specs GmbH) on both sides of the substrates. The substrates' unpolished sides were the ones in contact with the Ag paint. While XPS data taken on all polished surfaces and on the LAOTT2 and 3 unpolished ones reveal only the presence of La, Al, and O (and some C as impurity, coming from sample manipulation in ambient conditions), those taken on the unpolished surfaces of LAOTT4 and 5 show Ag3p and 3d as well as Fe2p signals. In LAOTT1 a signal coming from Ag was found but not from Fe. The higher concentration of Fe was found in LAOTT5, where it was almost 2% of the Al one.

To perform a more detailed element analysis we use the TXRF method available in the Laboratorio Nacional de Luz Sincrotron, Campinas Brazil. In this technique, x rays are made to impinge on the surface of the sample at grazing incidence such that total reflection occurs. The x rays excite atoms in the top layers of the material and the fluorescence is detected by a Si (Li) detector placed above the sample. TXRF can determine the concentration of transition metal impurities at levels above 5×10^{9} atoms/cm^2, when used with a conventional x-ray source. However, when used in combination with high brightness synchrotron radiation, detection limits can be improved to 8×10^{7} atoms/cm^2 for transition metals. Synchrotron radiation TXRF spectra of polished and unpolished surfaces of LAOTT1 are shown in Fig. 4. The spectrum of the unpolished side shows the lanthanum (L) fluorescence lines as well as the K_α and K_β Fe fluorescence lines. The same was observed for LAOTT 4 and 5. No iron lines were detected in both sides of LAO and LAOTT2 and 3.

In order to make a correspondence between the iron contamination and the magnetization found in these samples we performed a plot of magnetic moment of the LAO and LAOTTs at 0.2 T versus the ratio of the fluorescence iron K line areas to the lanthanum (L) ones. The result is shown in Fig. 5. As can be seen, a linear correspondence was obtained, indicating a direct correspondence between magnetism and iron contamination in these samples. The results obtained from two of our pure film samples (SnO_2 and TiO_2) are also included for comparison. These films were prepared time ago

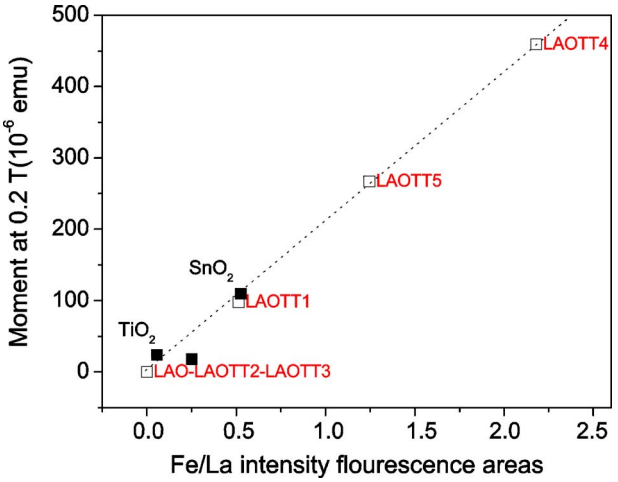

FIG. 5. (Color online) Plot of magnetic moment of the LAOs at 0.2 T vs the ratio of the fluorescence areas of iron K lines to lanthanum (L) ones.

and cleaned several times, previously to the measurements presented here. It can be seen that for these samples the magnetism could arise from the Fe contaminated commercial silver paint. In order to confirm this hypothesis, we prepared two additional films of pure SnO_2 in the same conditions of the just mentioned film (sample 1), one of them fixed to the silicon substrate in the oven using Ag paint A (sample 2, prepared before to perform the thermal treatment on LAOTT3) and the other one (sample 3) fixing the substrate without any Ag paint and on a substrate polished on both sides. The magnetic behaviors (discounting substrate signal) are shown in Fig. 6. We can see that the third film is completely diamagnetic and the second one presents very weak magnetism. In the inset we show both substrate and sample hysteresis loops, where it can be seen that both signals are barely distinguished from each other. Then, we may conclude that just diamagnetic behavior is observed in a SnO_2 film when no Ag paint is applied, strongly suggesting that ferromagneticlike hysteresis is not an intrinsic phenomenon in pure SnO_2 films.

In addition, x-ray absorption near edge spectroscopy in fluorescence yield, which is especially useful for the study of dilute samples, was employed in order to yield information about the phases that contain Fe in the LAOTT. The sample spectrum (not shown here) corresponds well in fine structure

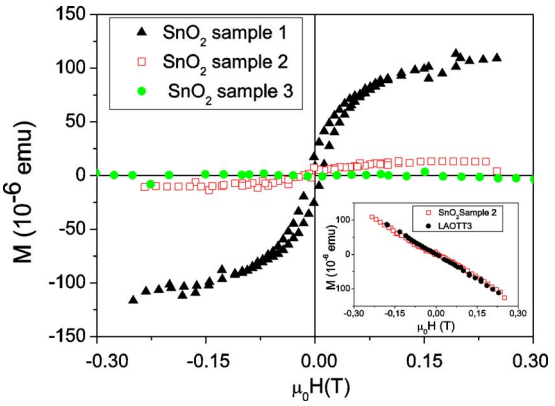

FIG. 6. (Color online) Magnetization loops of SnO_2 films prepared under different conditions. Sample 1: silver paint B used. Sample 2: silver paint A used. Sample 3: no silver paint used.

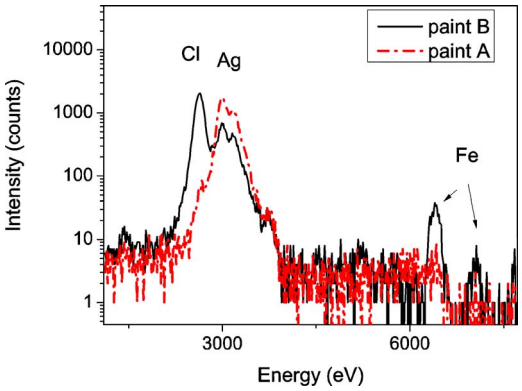

FIG. 7. (Color online) TXRF spectra of Ag paints named A and B in the text.

to the iron metal reference one, both below and above the Fe ionization potential. This qualitative comparison verifies that iron exists as clusters which are of metallic character.

Finally, in order to give a further confirmation that Fe in the magnetic substrates is a product of contamination with the Ag paint, we performed TXRF measurements on paints called A and B. The results (shown in Fig. 7) confirmed the presence of iron impurities in paint B which was the one employed to fit substrates LAOTT1, 4, and 5 to the oven, substrates which then resulted magnetic. It is worth noting that the iron containing paint TXRF measurement shows also evidence of Cl presence, suggesting that Fe could be in the form of Cl_3Fe.

In summary, we have studied $LaAlO_3$ substrates thermally treated with a procedure similar to those followed during real film deposition. Ferromagneticlike behavior was found in three of the substrates. Metallic iron impurities were detected in these substrates, product of contamination with the Ag paint used to fix the substrates to the silicon holders in the oven. The same conclusion applies to the magnetic behavior observed in our pure TiO_2 and SnO_2 films, strongly suggesting that ferromagneticlike magnetization loops recorded in these systems are of extrinsic origin.

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