Transparent Cr-doped SnO$_2$ thin films: ferromagnetism beyond room temperature with a giant magnetic moment

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Abstract
Laser ablated Cr-doped SnO_2 thin films grown on various kinds of substrates all show ferromagnetism well beyond room temperature. Surprisingly, films of $Sn_{0.95}Cr_{0.05}O_2$ grown on $LaAlO_3$ substrates have a giant magnetic moment of 6 μ_B/Cr, which is 20–30 times larger than that of films grown under the same conditions on $SrTiO_3$ and R-cut sapphire substrates. All films are highly transparent.

Since ferromagnetic semiconductors with high Curie temperature (T_C) are in great demand for application in spintronics, inducing ferromagnetism (FM) by doping transition metal into semiconducting oxides has been attempted by many research groups. Basically, the work has focused on doping Co, Fe, Ni, V, Cr into TiO_2 or ZnO [1–6]. Recently, Co and Fe have been used to dope SnO_2 and this has resulted in FM well beyond room temperature with very large magnetic moments (7.5 μ_B/Co and 1.8 μ_B/Fe for Co:SnO_2 and Fe:SnO_2 films, respectively) [7, 8].

In this paper, we report on FM above room temperature accompanying a giant magnetic moment in Cr-doped SnO_2 thin films. This very strong FM with a surprisingly large magnetic moment in compounds doped with non-ferromagnetic elements such as Cr is interesting. And together with the results obtained on V-and Cr-doped TiO_2 thin films [4, 5], this finding proves that doping a small amount of transition metal into non-magnetic oxides could induce room temperature FM.

220 nm thick $Sn_{0.95}Cr_{0.05}O_2$ films 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
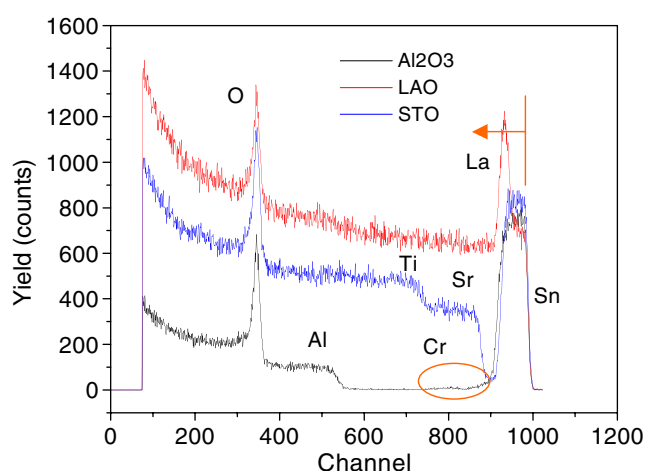
Figure 1. RBS spectra for $Sn_{0.95}Cr_{0.05}O_2$ films on three kinds of substrates.
(This figure is in colour only in the electronic version)

laser with $\lambda = 248$ nm) from a $Sn_{0.95}Cr_{0.05}O_2$ ceramic target made by the sol–gel method. 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_{O_2}) was kept at 10^{-4} Torr, and after deposition, films were cooled down to room temperature, under the same oxygen pressure as during deposition, with a rate of 20 °C min^{-1}. The structural study was done by means of x-ray diffraction (XRD) using a Seifert XRD 3000P. The magnetization measurements were performed with a Quantum Design superconducting quantum interference device (SQUID) system from 0 up to 0.5 T at a range of temperatures from 400 down to 5 K. The chemical composition was determined by Rutherford backscattering spectroscopy (RBS).

All Cr:SnO$_2$ films on the three kinds of substrates are highly transparent. RBS data showed that the width of the Cr signal is almost the same as that of the Sn signal; therefore we can say that Cr atoms are distributed rather uniformly and homogeneously in the SnO$_2$ matrix. RBS spectra of the Cr:SnO$_2$ films are shown in figure 1. For films grown on different substrates in the same run, basically there is no difference in distribution of dopant atoms; however note that for films on LAO substrate, more delicacy is needed to distinguish the peaks, since there is some overlapping between the La signal of the substrate and the Sn signal of the film. The heights of the Cr and Sn peaks remain almost constant from the right to the left, showing that both Cr and Sn atoms are localized uniformly throughout the whole thickness of the film. From XRD patterns (see figure 2), one can see that Cr-doped SnO$_2$ films are basically formed as rutile. In the case of STO and LAO substrates, the 101 peak of rutile is prominent, while in the case of Al$_2$O$_3$ substrate, the most revealed peak is 110. For films on STO and Al$_2$O$_3$, the out-of-plane parameters are 2.32 and 2.64 Å, respectively (note that the parameters for bulk SnO$_2$ are $a = 4.738$ Å and $c = 3.187$ Å, tetragonal) [9].

The temperature dependence of the magnetization taken at 0.5 T for the Cr:SnO$_2$ film on LAO is shown in figure 3. One can see that the sample has T_C above 400 K, the magnetic moment remained almost constant for the whole range of temperatures below T_C and the saturation magnetization is surprisingly large, about 6 μ_B/Cr (determined from the saturated magnetic moment of the film with the size of 0.25 cm^2 as 5×10^{-4} emu, divided by the number of atoms of Cr on the film, from RBS data). There is no anomaly in the low temperature
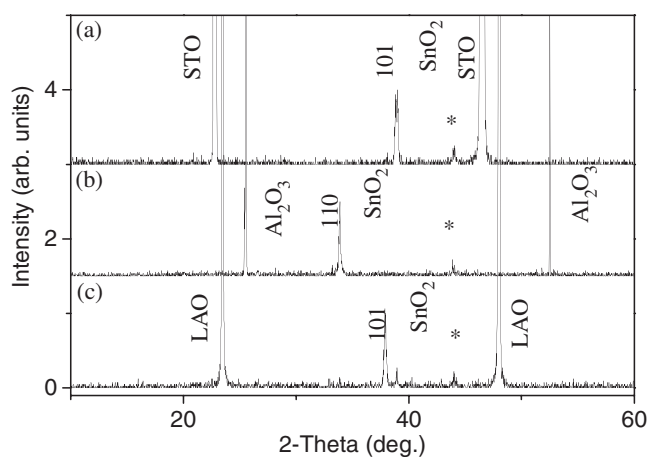
Figure 2. XRD spectra of Sn$_{0.95}$Cr$_{0.05}$O$_2$ films on (a) SrTiO$_3$, (b) Al$_2$O$_3$ and (c) LaAlO$_3$ substrates. The asterisk (*) marks the peaks of the sample holder.
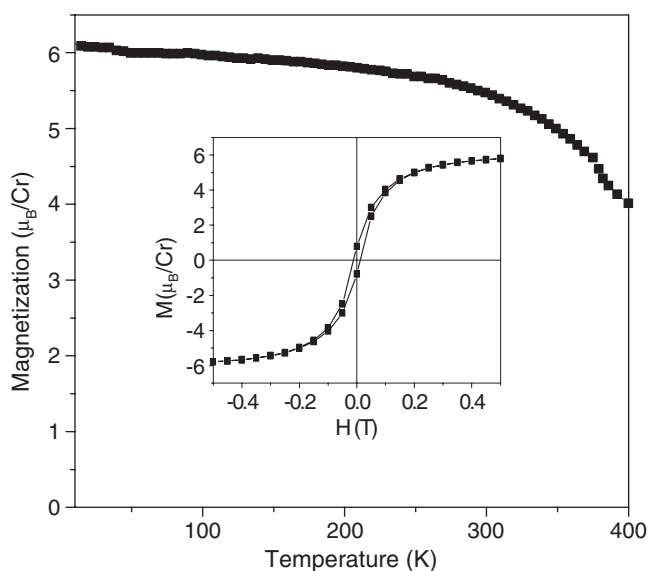

Figure 3. Magnetization versus temperature taken at 0.5 T for a Sn$_{0.95}$Cr$_{0.05}$O$_2$ film on LaAlO$_3$ substrate. The inset shows the M–H curve taken at 300 K.

region of this M–T curve, and no difference between the zero-field cooling and field cooling measurements observed, and this rules out the assumption of the existence of some clusters [10]. The room temperature FM is also confirmed by the field dependence of the magnetization taken at 300 K which shows a very well-defined hysteresis loop (see the inset of figure 3). The large value of M_s, 6 μ_B/Cr, could not come from Cr metal clusters because Cr metal is known to be paramagnetic at high temperatures and antiferromagnetic below 308 K. The T_C and M_s values of Cr:SnO$_2$ films (larger than 400 K and 6 μ_B/Cr, respectively) do not match the values for CrO$_2$ either (CrO$_2$ has T_C = 386 K and M_s = 2.03 μ_B/Cr) [11]; thus it is not possible to assume that the FM in the film comes from CrO$_2$ clusters (also recall the XRD data with no peak for CrO$_2$). The result is reproducible because the observed difference in magnitude of

the magnetizations of the three films fabricated under the same conditions in three different runs is negligible. One may question whether there is some diffusion between the film and the LAO substrate resulting in an La–Cr based compound which may give some signal of ferromagnetism. From the RBS data shown earlier, it is not possible to rule out completely the possibility of a small amount of La diffusing into the Cr:SnO$_2$ film on LAO since, from the RBS spectrum of the Cr:SnO$_2$ film on LAO, one can see a very small signal which cannot be seen for the Cr:SnO$_2$ film on Al$_2$O$_3$—on the right-hand side of the Sn peak. Its position might correspond to La in the film. Supposing that the Cr:SnO$_2$ film contains La, then our careful simulation gives a ratio for Sn:Cr:La as of about 300:18:2. Thus, the amount of La–Cr intermetallic compound, if any exists, should be very small, and it cannot be the origin of the large magnetization that was observed experimentally. The giant magnetic moment obtained in Cr:SnO$_2$ on LAO is worth noting when verifying the nature of the FM in those films. For Ni:SnO$_2$ films fabricated under exactly the same growth conditions as the Cr:SnO$_2$ films, the maximum M_s obtained is only 2 μ_B/Ni, even though Ni itself is ferromagnetic [12][4]. Thus, one can see that in comparison, in fact, doping with a non-ferromagnetic element may result in a much larger magnetic moment. This is similar to what was obtained for V/Cr-doped TiO$_2$ films [4, 5], proving that the induced FM does not depend simply on the magnetic ordering of the dopant itself. It seems that in these cases, there should be several mechanisms that co-govern the system at the same time (they may relate to anisotropy, defects, oxygen vacancy, etc) and the local spin density approximation (LSDA) alone cannot explain everything perfectly.

Interestingly, the giant magnetic moment is not obtained in Cr:SnO$_2$ films grown under the same fabrication conditions on STO and Al$_2$O$_3$ substrates (note that the three substrates were fixed at the same time in one run). Even though films on those two kinds of substrates are definitely FM above room temperature (figure 4), the magnitude of the magnetic moment is 20–30 times smaller than that of films on LAO, with M_s about 0.27 μ_B/ Cr and 0.2 μ_B/Cr for films on STO and Al$_2$O$_3$, respectively (note that the saturated magnetic moment of the film of the same size as the films on the LAO substrates is one order smaller, 2.32×10^{-5} emu). These values are rather modest, but almost as large as those of Co:TiO$_2$ films on LAO and STO [1, 13, 14]. The M–T curves of these films on STO and Al$_2$O$_3$ show a tendency to rise at very low temperatures (below 30 K), which suggests the possibility of some clusters existing in the films, according to [10]. If some antiferromagnetic precipitations (for example, from nanometre-sized Cr metal particles, which might be present below the detection limit of XRD of less than 5%) exist, their contributions could be the reason for a reduction of the magnitude of the magnetic moment in these two cases. One may also look for the reason for this big difference of magnetic moment in the kinds of strains of the substrates. As we know, the lattice parameter of LAO is $a = 0.3788$ nm, while that of STO is $a = 0.3905$ nm; the strain for LAO is compressive and that for STO is tensile. However, since no clear difference could be found between the lattice parameters of Cr:SnO$_2$ films on LAO and STO, it is not possible to explain the findings from the viewpoint of induced strains. On the other hand, from the topography images, we observed a big difference between the surface morphologies of LAO and STO substrates, which could elucidate the issue. The LAO substrate was seen as very flat, while the STO was seen as very rough, with a lot of steps on it. This may arise because, when the films are deposited on STO substrates, there is more chance for precipitations to form, and that might lead to a reduction of magnetic moment that we mentioned earlier. From another viewpoint, one can always state that there is a difference in dielectric constant of the films and the substrates, so for different substrates, there are always some induced different polarization

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[4] Under the same growth conditions, Ni:SnO$_2$ films on LAO have an M_s of 2 μ_B/Ni, while films on STO and Al$_2$O$_3$ have M_s values one order smaller, about 0.2 μ_B/Ni.
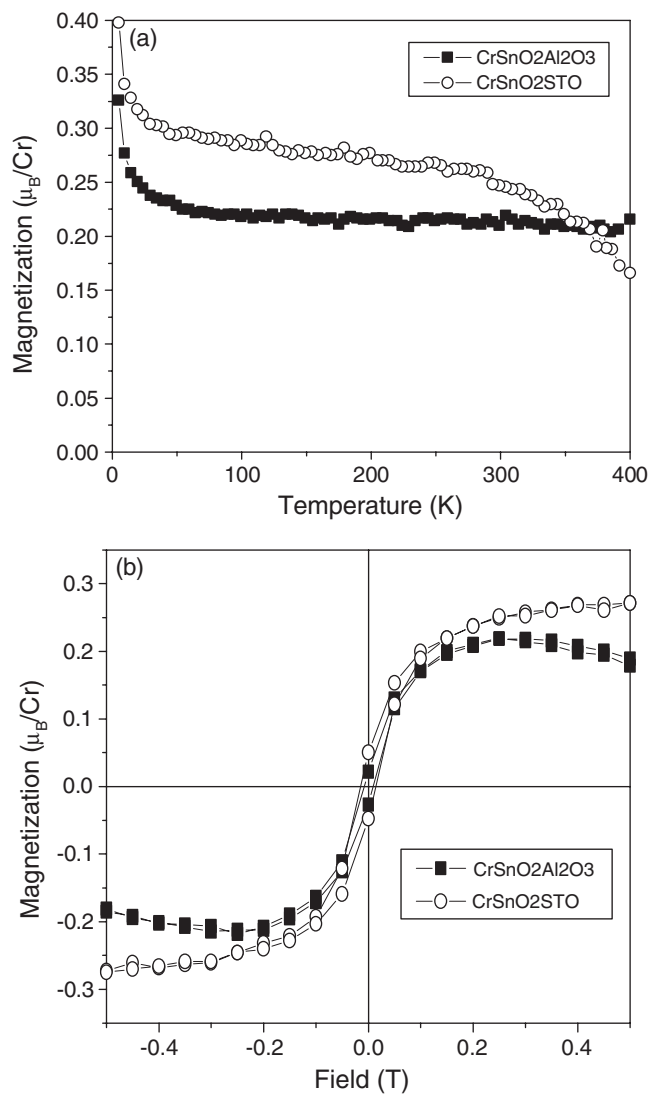
Figure 4. Magnetization (a) versus temperature at 0.5 T and (b) versus magnetic field at 300 K for Sn$_{0.95}$Cr$_{0.05}$O$_2$ films on SrTiO$_3$ and Al$_2$O$_3$ substrates.

effects and electric gradients in the films that may contribute somewhat to the difference in magnetism.

Thin films of Cr-doped SnO$_2$ on various kinds of substrates all show ferromagnetism above room temperature. Films of Sn$_{0.95}$Cr$_{0.05}$O$_2$ grown on LaAlO$_3$ substrates have a giant magnetic moment of 6 μ_B/Cr, much larger than that of films grown under the same conditions on SrTiO$_3$ and R-cut sapphire substrates. That can be seen directly when comparing the values of magnetic moments of films on LAO and on STO and Al$_2$O$_3$ with the same size of the substrates, which are one order different (before taking into account the number of dopant atoms in the films). From the viewpoint of structural analysis, at the moment there is no explanation of a difference of the substrates that could result in a big difference in magnetic

moment. However, we assume that in the case of $SrTiO_3$ and Al_2O_3 substrates, there might be some antiferromagnetic precipitations of Cr particles which might contribute to the magnetism of those films and, as a consequence, reduce their ferromagnetism. In the case of $Cr:SnO_2$ films on $LaAlO_3$ substrates, the giant magnetic moment which probably comes from the doped matrix is remarkable.

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