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Citation: Applied Physics Letters **89**, 012501 (2006); doi: 10.1063/1.2219145
View online: http://dx.doi.org/10.1063/1.2219145
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/89/1?ver=pdfcov
Published by the AIP Publishing

Search for ferromagnetism in conductive Nb:$SrTiO_3$ with magnetic transition element (Cr, Co, Fe, Mn) dopants

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(Received 10 April 2006; accepted 16 May 2006; published online 5 July 2006)

Thin films of (0.5%, 1%) Nb:$SrTiO_3$ dilutely doped with (2 at. %) magnetic transition elements (Cr, Co, Fe, Mn) are examined for ferromagnetism. X-ray diffraction, Rutherford backscattering ion channeling, scanning transmission electron microscopy Z-contrast imaging, and electron energy loss spectroscopy techniques establish high crystalline quality of the films with no impurity phase(s) and highly uniform dopant distribution. Although the film conductivity improves dramatically by Nb doping, no ferromagnetism is found in any of our samples over the temperature range of 365 down to 5 K. This is contrasted to the case of ferromagnetism reported in cobalt doped (La,Sr)TiO_3.
 [DOI: 10.1063/1.2219145]

In recent years, search for intrinsic high Curie temperature diluted magnetic semiconductors (DMSs) has become a fascinating endeavor in the context of the emerging field of spintronics.[1,2] Intrinsic DMS has been successfully achieved in magnetic ion doped III-V semiconductors;[3] however, the Curie temperature (T_c) of this class of materials is too low to be used in practical applications. Interestingly, above room temperature ferromagnetism (FM) has been reported in magnetic impurity doped oxides, for instance, Co–TiO_2,[4,5] Co–ZnO,[6] Co–Cu_2O,[7] etc., but the intrinsic origin of FM in these systems continues to be controversial due to secondary phases and dopant clusters encountered under different growth conditions.[8–11] Even in cases wherein the films seem to be free of defects and clusters the mechanism of FM is still under debate.

A few years back, we had discovered above room temperature FM in Co–(La,Sr)TiO_3 (LSTO) and suggested that this system is an intrinsic DMS.[12] Recently, a spin polarization of about 80% was reported in Co–LSTO supporting the intrinsic nature of DMS-FM in this system.[13] Since the insulating Co–$LaTiO_3$ and Co–$SrTiO_3$ do not show any FM,[14] the FM in conductive Co–LSTO is attributed to carriers.[12,13,15] Inaba and Katsufuji[16] have suggested FM exchange interaction between Cr spins via carriers in the Cr–LSTO system. These studies raise an interesting question: can ferromagnetism be induced in magnetically doped $SrTiO_3$ (STO) by other means of carrier doping?[16,17] It is well known that niobium, as a donor impurity, can also introduce large number of carriers into STO conduction band.[18–20] Although this is similar to La doping, it should be noted that La substitutes Sr (rare earth site) while Nb substitutes Ti. Therefore we examine in this work the possibility of FM interaction between magnetic transition element (MTE) (Cr, Co, Fe, Mn) doped conducting Nb:STO. A STO based DMS is important because of its perovskite structure which lends itself to epitaxial integration with many functional oxides.

The 2%MTE (Cr, Co, Fe, Mn) and (0.5%, 1%) niobium dual doped STO thin films were grown on $LaAlO_3$ (001) (LAO) by pulsed excimer laser deposition (KrF, $\lambda=248$ nm, $E=2$ J/cm^2, and $f=10$ Hz) at 870 °C. The oxygen partial pressure was $\sim 10^{-6}$ Torr. The films were characterized by x-ray diffraction (XRD), Rutherford backscattering (RBS) ion channeling, four probe resistivity, magnetization measurements, scanning transmission electron microscopy (STEM) Z-contrast imaging, and electron energy loss spectroscopy (EELS).

A typical XRD pattern for a dual doped film on LAO is shown in Fig. 1(a). No impurity phase is present and the film orientation is (001) with a perovskite structure. The rocking curves has a full width at half maximum (FWHM) below 0.2° for all the films, indicating a high degree of crystallinity. Moreover, with increasing niobium concentration the (002) film peak is seen to shift to lower 2θ (not shown), implying increase of lattice parameter c and substitutional incorporation of niobium into the STO lattice.

Rutherford backscattering data confirm the excellent quality of our thin films. Figures 1(b) and 1(c) show the RBS (random and channeled) spectra for 2%Cr, 0.5%Nb and 2%Co, 0.5%Nb doped $SrTiO_3$ films, respectively. The elemental positions are indicated on the spectra. The strontium minimum yield for the Co doped one is ~8%, and for the Cr doped one is even lower (~4.5%), indicating high dopant substitutionality and small lattice distortion disorder. The pure niobium doped STO films prepared at the same condition recently by our group showed a similar minimum yield,[20] which means that the quality of the thin films is not affected by magnetic transition element doping.

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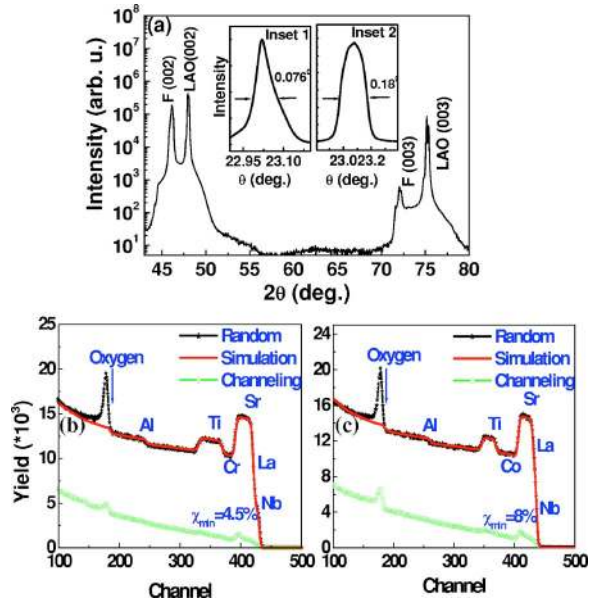

FIG. 1. (Color online) (a) A typical θ-2θ XRD pattern for 2%MTE, Nb:STO thin films on $LaAlO_3$ (001). Peaks labeled "F" correspond to the film. Inset 1 shows the XRD rocking curve for a thin film with chromium doping. Inset 2 shows the rocking curve for a cobalt doped one. [(b) and (c)] 3.05 MeV He^+ Rutherford backscattering (RBS) random simulation and channeling spectra for the 2%Cr, 0.5%Nb doped STO and 2%Co, 0.5%Nb doped STO thin films, respectively.

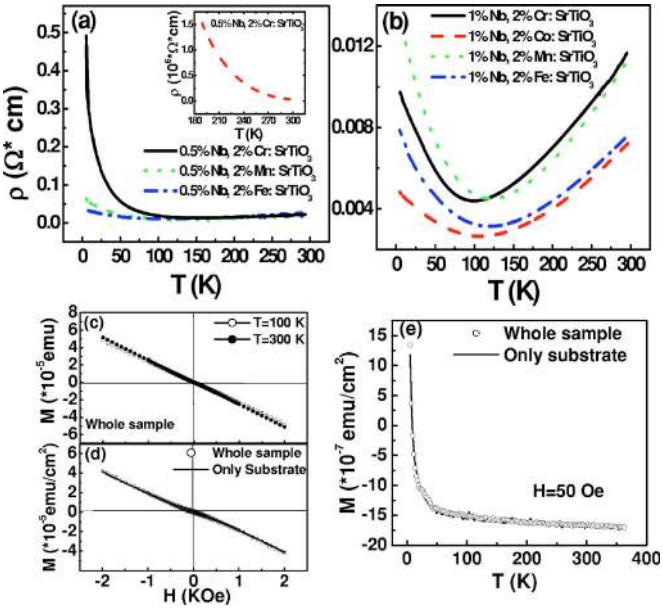

FIG. 3. (Color online) [(a) and (b)] Temperature dependence of resistivity for these thin films: 2%MTE, 0.5%Nb doped STO and 2%MTE, 1%Nb doped STO, respectively. (c)Typical M vs H for one thin film (including substrate) at 300 and 100 K. (d) Comparison of M-H for one sample with a heated pure substrate at 15 K. (substrate area unity: emu/cm^2). (e) Comparison of M-T for one sample with a heated pure substrate at an applied field of 50 Oe.

Figure 2(a) shows the STEM Z-contrast imaging for the 2%Cr, 0.5%Nb doped STO thin film, which is featureless and has no clusters. The high resolution micrograph shown in Fig. 2(b) also brings out the epitaxy and good interfacial quality of the film, consistent with the RBS channeling data. The uniformity of elemental distribution in the film was studied by probing the film cross section via tens of EELS line scans. A typical series of line scans covering oxygen and chromium (shifted in the y direction for clarity) is presented in Fig. 2(c). The first two signals (bottom two lines) were recorded on LAO and the interface, respectively, while the rest in the film region. Figure 2(d) shows the EELS analysis

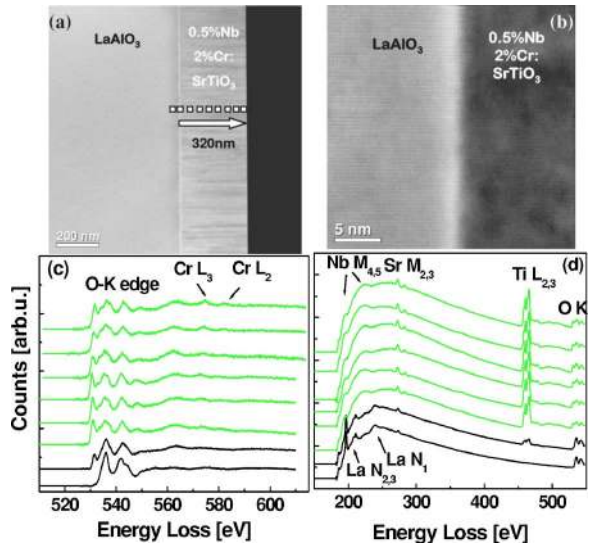

FIG. 2. (Color online) (a) Cross sectional TEM image at large length scale of the 2%Cr, 0.5%Nb doped STO film grown on $LaAlO_3$ (001) substrate. (b) High resolution TEM image for the interface between the film and substrate. [(c) and (d)] EELS line scans across the cross section of the sample.

covering lanthanum, strontium, titanium, oxygen, and niobium contributions. As the probe crosses the interface, the La $N_{2,3}$, N_1 edge disappears while the Ti $L_{2,3}$, Sr $M_{2,3}$, and Nb $M_{4,5}$ edges are consistently present in the film. The intensity of each signal does not change inside the thin film, indicating a uniform distribution of all the elements. Similar STEM and EELS results also obtained in other samples suggest that these thin films indeed have very good quality with all elements uniformly distributed in the lattice and they are free of any type of clusters.

The temperature dependences of resistivity for 2%MTE, 0.5%Nb:$SrTiO_3$ and 2%MTE, 1%Nb:$SrTiO_3$ are given in Figs. 3(a) and 3(b), respectively. Clearly, Nb doping induces conductivity in STO. For 0.5%Nb doping, only the cobalt doped film shows semiconductor behavior over the entire temperature range, while the other three samples show metal to semiconductor transition at around 120 K during cooling. For 1%Nb doping [Fig. 3(b)], all four samples show metal to semiconductor transition during cooling. Although no obvious shift of transition temperature is seen, the resistivity of each film is much lower than that for the corresponding 0.5% Nb doping case. The details regarding the origin and systematic of the metal-insulator transition will be discussed separately.

Though the samples show excellent quality and good conductivity, it is found that none of them exhibits any ferromagnetism from 365 down to 5 K. Figure 3(c) shows the typical field dependence of magnetization obtained at 300 and 100 K. Obviously, no FM is observed, the linear negative signal being the diamagnetic substrate contribution. Figure 3(d) shows the M-H loop taken at 15 K. We have calculated the magnetic moment per cm^2 of our sample (thin film together with substrate) and compared it with the signal of a heated (similarly processed, but for film deposition) substrate. Both the sample and substrate show hysteresis loops,

and these loops overlap with each other. This means that the FM observed at this temperature is totally from the substrate, an extrinsic contribution. Furthermore, we measured the temperature dependence of magnetic moment over the entire temperature range of 365 to 5 K. As shown in Fig. 3(e) our sample (per cm^2) has the same magnetic moment as the substrate (per cm^2). Therefore, it is believed that no FM occurs in the magnetic transition element and niobium dual doped $SrTiO_3$ thin films.

Tracking back to the origin of magnetic interaction in recently burgeoning diluted doped conductive systems, the most commonly used approach is of a Ruderman-Kittel-Kasuya-Yosida (RKKY)-type carrier mediated one,[21–23] where the numbers of spins and carriers are the most important parameters for the coupling between spin and charge degrees of freedom. Theoretically, the RKKY interaction can be written by the following formula:

$$J \sim \frac{\sin(2k_F r) - 2k_F r \cos(2k_F r)}{(2k_F r)^4}, \tag{1}$$

where distance between spins r is $\sim n_s^{-1/3}$ [n_s is the density of local moments determined by the magnetic dopant concentration (x)]. The Fermi wave number k_F is $\sim n_c^{1/3}$ [n_c is the carrier density determined by donor impurity level (y)]. For $n_c \ll n_s$, the Weiss mean-field treatment will lead to the ferromagnetic RKKY interaction, and the FM exchange strengthens with the increase of n_c up to the $\sim n_s$ value.[22,23] Since one Nb donor provides less than one electron[19] the carriers induced by Nb should be less than yN_{Ti}, where $y = 0.5\%$ or 1% in our samples and N_{Ti} is the titanium concentration in undoped STO. We also consider the carriers contributed by possible oxygen vacancies. As pointed out by Leitner *et al.*,[19] the carriers induced by oxygen vacancies in the thin film grown at $\sim 1\times 10^{-8}$ Torr and 870 °C have less than 10% contribution. So spin density given by $2\%N_{\mathrm{Ti}}$ should be much higher than the carrier density. Experimentally, it is found that around 1%Nb doping even together with high oxygen reduction into STO produces less than 10^{20} cm^{-3} carriers.[19] Given the STO lattice parameters, $a = b = c = 3.905$ Å, the titanium concentration in undoped STO is $\sim 1.6\times 10^{22}$ cm^{-3} and hence the spin density of $2\%N_{\mathrm{Ti}} \sim 3.2\times 10^{20}$ cm^{-3} which is several times higher than the carrier density. Thus the RKKY interaction in our samples should be ferromagnetic. It should be noted that the antiferromagnetic superexchange (SE) interaction as a short range type is unlikely to happen in our dilutely doped system with only 2%MTE uniformly distributed. On the other hand, for the reported FM Co–LSTO system,[12,13] the carrier density n_c is around 10^{22} cm^{-3} which is much higher than the spin density $n_s \sim 3.2\times 10^{20}$ cm^{-3}. In this case, the frustration effects in RKKY oscillation become important and should lead to the collapse of FM interaction.[22,23] Therefore, the finding of FM in Co–LSTO and its absence of FM in our magnetic transition element doped Nb:STO may indicate that the RKKY-type carrier mediated interaction is not adequate to explain the origin or absence of magnetism in these oxide-based conductive systems. Indeed, in oxide-based DMS, new mechanisms such as F-center model[24] and polaronic percolation theory[25] have been put forward and may need to be considered.

In conclusion, magnetic transition element (Cr, Co, Fe, Mn) and niobium dual doped $SrTiO_3$ epitaxial films were grown by pulsed laser deposition. XRD, RBS, STEM Z-contrast imaging and EELS together establish excellent film quality with highly orientated epitaxial growth, absence of clusters or secondary phases, and uniformity of dopant distribution. No evidence for the occurrence of ferromagnetism is observed at the temperature range from 365 down to 5 K.

The financial support for this work by DARPA Spin S program, NSF-MRSEC Grant Nos. DMR-00-80008, DMR-05-20471, and DMR-0335364, and DOE Grant No. DOE-DE-AC02—05CH11231 is gratefully acknowledged.

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