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Corrigendum

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Peng and John Q Xiao 2008

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It has come to the attention of the authors that they omitted an author from the author list of the above article. The excluded author, Dr Lubna R Shah (Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA), made a critical, important contribution to the work reported in the paper. The authors apologise for this oversight and gratefully acknowledge Dr Shah's contribution to this work.

Direct evidence of oxygen vacancy mediated ferromagnetism of Co doped CeO₂ thin films on Al₂O₃(0001) substrates

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Abstract

Thin films of room temperature diluted magnetic oxides (DMO) of Co doped CeO₂ (Ce_{0.97}Co_{0.03}O_{2- δ}) with a predominant orientation of (001) have been deposited on Al₂O₃(0001) substrates. An Ar⁺ sputtering process has been applied to the as deposited films to investigate its effect on the films' ferromagnetic properties. With the aid of magnetic measurements, we find that Ar⁺ bombardment has an obvious effect on the magnetic properties of the as deposited films, i.e., the saturated magnetization moments (M_S) are enhanced by Ar⁺ bombardment. More detailed work has been done to further explore the inherent mechanism. Ar⁺ sputtering was found to introduce additional oxygen vacancies (V_O) into the as deposited films (through x-ray photoelectron spectroscopy and Raman spectral analysis), which should make a certain contribution to the enhanced M_S observed for Ar⁺ sputtered films. The experimental results provide direct evidence of V_O enhanced ferromagnetism of insulating DMO, and are consistent with the recently proposed F-center exchange coupling mechanism.

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

1. Introduction

Diluted magnetic oxides (DMO) with high Curie temperature (T_C) have been reported recently for transitional metal (TM) doped semiconducting [1–3] or insulating [4, 5] oxides. But the intrinsic origin of the observed ferromagnetism (FM) remains controversial. The ever more widely accepted carrier mediated FM mechanism [1], which is responsible for the FM in TM doped semiconducting oxides, is now being challenged by the discovery of high temperature FM in TM doped insulating oxides, which relates to an oxygen vacancy (V_O) mediated FM mechanism [3, 6] or so-called F-center exchange coupling (FCE) mechanism instead. According to this mechanism, it is the F-centers, which consist of an electron trapped in a V_O , acting as the coupling centers, via which doped magnetic ions align in ferromagnetic order. Invoking to this mechanism, many researchers have reported that annealing the doped oxide in reducing atmosphere (H_2 flow

or vacuum) distinctly enhanced its magnetization [7–9], while annealing in an oxidizing atmosphere (air or oxygen flow) could significantly depress the FM [10–12]. Even the oxygen pressure during film growth has a notable effect on the magnetic behavior, as observed by Vodungbo *et al.*, for Co doped CeO₂ film [13]. These results seemingly agree with the FCE mechanism very well. But reduced annealing or depositing of films at low oxygen pressure cannot preclude the formation of undetectable magnetic metal or clusters, which can also result in the enhancement of ferromagnetism. Thus this ambiguous evidence could not be considered arbitrarily as direct confirmations of the FCE mechanism. A direct relation between magnetic behaviors and V_O has not been established experimentally yet. Very recently, Co doped CeO₂ [5, 13, 14] films with giant moments of about $7 \mu_B/\text{Co}$ and T_C well above room temperature (RT) have been successfully fabricated on Si and other substrates. Discovery of such FM at high temperature in dielectric films paves the way for the realization of novel

spin filters to be used in actual spintronic devices, such as spin transistors [15–18] or spin filter devices [19, 20]. CeO₂ is an insulating material with high dielectric constant (as high as 26 for single-crystal CeO₂). Therefore, the discovery of FM in Co doped CeO₂ systems is highly likely to be attributable to V_O according to the FCE mechanism. If this is the case, the magnetization in Co doped CeO₂ would readily be changed according to the variation of V_O density. But as far as we know at present, little work has been done on this aspect. The Ar⁺ sputtering method is known as an effective way to introduce V_O into CeO₂ as a preferential release of oxygen occurs during the process [21].

In this paper, Co doped CeO₂ thin films with the stoichiometry of Ce_{0.97}Co_{0.03}O_{2-δ} were prepared, and parts of samples were subjected to Ar⁺ sputtering for different periods of time. In this instance the V_O density in the as deposited films is progressively changed, while other phase separations can be totally avoided. With the characterization of V_O density and the corresponding magnetic properties, the experimental results genuinely indicate that V_O has a decisive influence on the magnetic property, and thus provide a straightforward confirmation of the FCE mechanism, which is still the mostly supposed theory for explaining the FM origination in TM doped insulating DMO.

2. Experiment

Co doped CeO₂ films with the stoichiometry of Ce_{0.97}Co_{0.03}O_{2-δ} were deposited on Al₂O₃(0001) substrates by a long range magnetron sputtering method. The highly dense target used here was prepared from a CeO₂ (99.99%) and CoO (99.99%) mixture by the standard solid reaction method. The target was sputtered in a background vacuum of 10⁻⁶ Pa, onto Al₂O₃(0001) substrates which were preheated to 723 K. During the deposition process, the target–substrate distance (TSD) was kept at about 40 cm. This long distance, which is much larger than the usual TSD adopted in magnetron sputtering, makes the growth rate slow enough to lead to as deposited films of high quality. In fact, films about 1 μm in thickness were obtained by sputtering for 20 h with the power of 60 W in our experiment. In order to diminish the departure of the oxygen content from the nominal stoichiometry in the as deposited films, an O₂ flux of 20 sccm was injected into the chamber during film deposition. Structures were analyzed using x-ray diffraction (XRD, Bede TM 2000) with Cu Kα radiation. Ar⁺ sputtering was carried out in an x-ray photoelectron spectroscopy (XPS) chamber which operates at 300 V ionic voltage and 2000 V accelerating voltage, with 1 × 10⁻⁶ Torr of Ar, giving a current density of 100 μA cm⁻². XPS characterization was achieved *in situ*, after the Ar⁺ sputtering process. Then Raman spectra measurements were performed using a Jobin Yvon LabRamHR spectroscope in vacuum at RT. The 532 nm line was used as the excitation source, with spectral resolution 4 cm⁻¹. The power density was kept under 2 mW, which is low enough to avoid heating effects on samples. Magnetic properties were measured at RT using a commercial vibrating sample magnetometer (VSM, Model BHV-525) with a resolution of 1 × 10⁻⁶ emu. Both the Raman

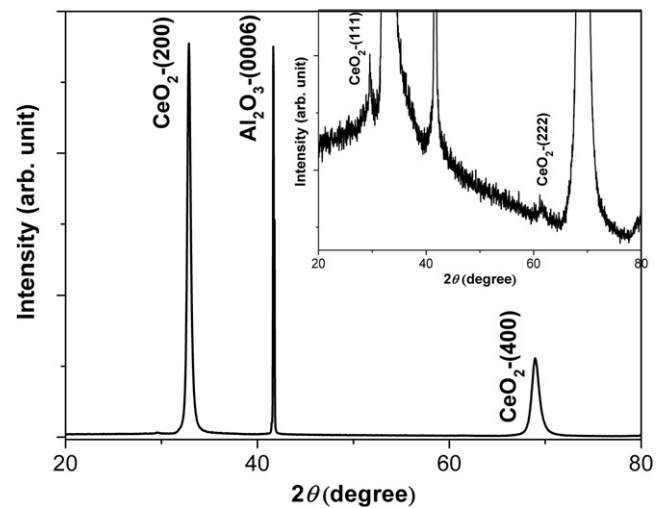


Figure 1. Typical XRD pattern for the as deposited Ce_{0.97}Co_{0.03}O_{2-δ} films on Al₂O₃(0001) substrates. The inset shows a scaled-up part to show the low intensity of CeO₂ (111) orientation.

and magnetic measurements were performed immediately after the Ar⁺ sputtering process.

3. Results and discussion

Typical XRD patterns of the as deposited film are shown in figure 1. It indicates that the as deposited films have good crystalline quality and good preferential orientation along the (100) direction, with very small weight of (111) orientation as shown in the inset. There is no any evidence of other impurity phases, rather than CeO₂ fluorite structure.

To further validate the phase purity of the as deposited Ce_{0.97}Co_{0.03}O_{2-δ} films, XPS characterization of the Co 2p spectrum has been carried out. As shown in figure 2, a linear background subtraction is performed on the raw data, and the peaks are fitted using a Gaussian method. The resulting Co 2p_{3/2} and 2p_{1/2} core levels for Co–O bonding are found to be at 779.98 eV and 796.31 eV, respectively. This XPS features, according to Zhang [22], excludes the possibility of Co cluster formation. Besides, two strong shake-up satellites, as labeled in figure 2, emerge at high energy levels of Co 2p_{3/2} and 2p_{1/2}, which affords typical evidence for bivalent cobalt ions existing in the as deposited Ce_{0.97}Co_{0.03}O_{2-δ} films.

As indicated in figure 3, the as deposited films are ferromagnetic, with saturated magnetization (M_S) of about 1.0 μ_B/Co and a coercive force (H_C) about 70 Oe at RT. Its T_C is above RT as seen from the magnetization versus temperature ($M-T$) curve shown in the inset. The $M-T$ measurement was carried out using a commercial superconducting quantum interference device (SQUID) in a field of 1 kOe. The intrinsic FM in low Co doped CeO₂ compounds, both in film and bulk forms, has been confirmed in several experimental works [5, 13, 14]. But the origination mechanism of the FM in these insulating DMO is still ambiguous. As mentioned in the introduction above, the recently proposed FCE mechanism relates to an oxygen vacancy mediated FM.

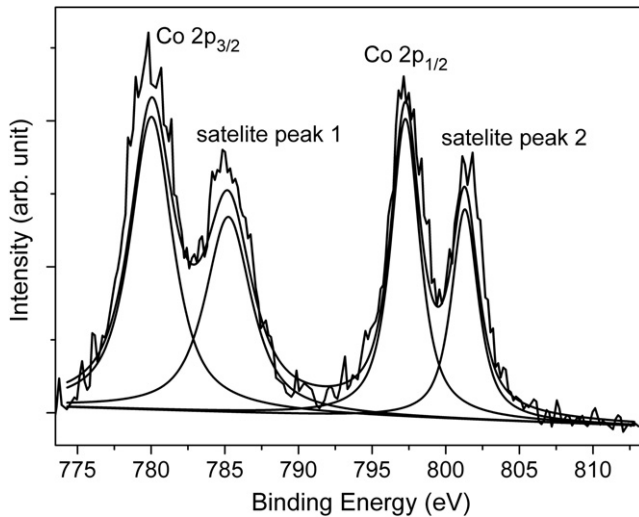


Figure 2. Co 2p XPS for the as deposited $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ films on $\text{Al}_2\text{O}_3(0001)$ substrate.

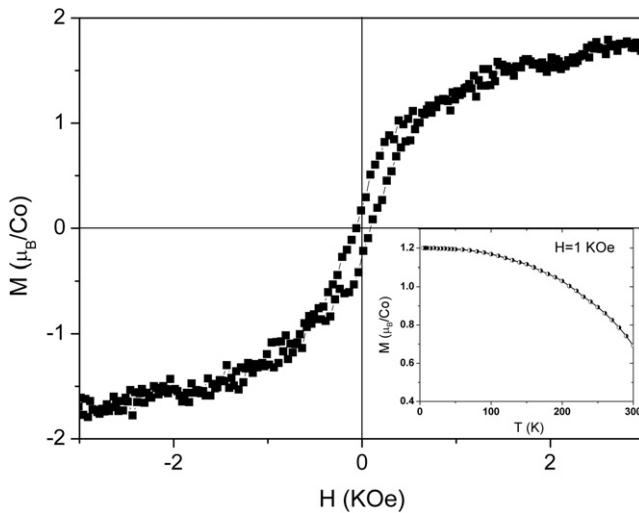


Figure 3. M - H loop of the as deposited $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ film, and the corresponding M - T curve shown in the inset.

According to FCE mechanism, the doped Co ions as well as V_O are two necessary requirements resulting in the FM in Co doped CeO_2 . Thus keeping the content of the doped Co ions as a constant, the FM would be enhanced according to the V_O density. In the following context we have tried to provide an experimental confirmation of this mechanism. In order to introduce additional V_O into Co doped CeO_2 films, some of the as deposited films were subjected to Ar^+ sputtering for different periods of time. After each sputtering process, the V_O density and the corresponding magnetic moments of each sample were characterized and compared.

V_O density could be reflected by Ce 3d and O 1s XPS spectra in CeO_2 [23]. As is well known, with oxygen deficiency, Ce^{4+} would be reduced to Ce^{3+} in CeO_2 while still retaining its fluorite structure, i.e., $2\text{Ce}^{4+} + 2e \rightarrow 2\text{Ce}^{3+} + \text{V}_\text{O}$. Thus one would obtain the density of V_O in CeO_2 comparatively by comparing Ce^{3+} relative weights.

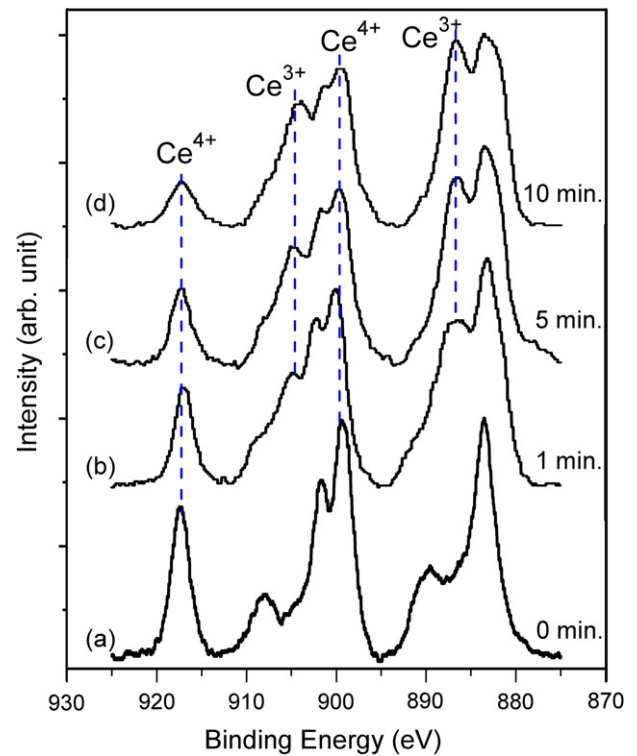


Figure 4. Ce 3d photoemission spectra of $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ films subjected to Ar^+ sputtering for the indicated periods of time, in which the positions corresponding to Ce^{3+} and Ce^{4+} are labeled.

Figure 4 presents the changes in the Ce 3d XPS spectra of $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ films sputtered with Ar^+ for different periods of time. A linear background subtraction is performed on all the raw data. These spectra were analyzed according to [24]. As indicated in figure 4, the main peaks for $\text{Ce}^{4+} 3d_{3/2}$ and $\text{Ce}^{4+} 3d_{5/2}$ are designated at binding energies of 916.9 eV and 898.3 eV, respectively. Those of $\text{Ce}^{3+} 3d_{3/2}$ and $\text{Ce}^{3+} 3d_{5/2}$ are indicated at 903.9 and 886.4 eV. It can be seen that the intensity of $\text{Ce}^{3+} 3d$ peaks, as indicated in figure 4, apparently increases with the increasing of the Ar^+ sputtering time, implying an increased amount of V_O with reduction of ceria.

O 1s XPS spectra are used as another source of information about V_O density. In $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$, O 1s spectra show the contributions from $\text{Ce}^{4+}\text{-O}$, $\text{Ce}^{3+}\text{-O}$, and $\text{Co}^{2+}\text{-O}$ bonded species. We do know that the O 1s peak from $\text{Co}^{2+}\text{-O}$ bonds should be at higher binding energy than that of the O 1s peak from Ce-O bonds, as Co has a higher electronegativity (1.88 on the Pauling scale) than Ce (1.12). One would expect 1s electrons in oxygen attached to cerium atoms in the (+3) oxidation state to be more tightly bound than for cerium in the (+4) state. But the spectrum can be well fitted with two Gaussian peaks as shown in figure 5. The position, height, and full width at half-maximum (FWHM) were all varied to obtain the fit. It can be reasonably supposed that the intensity of the individual peak corresponding to $\text{Co}^{2+}\text{-O}$ bonds is very low and was covered up due to the low Co concentration. According to the above analysis, peaks A and B are from $\text{Ce}^{4+}\text{-O}$ and $\text{Ce}^{3+}\text{-O}$ species, respectively. Examining the relative areas of peaks A and B gives an

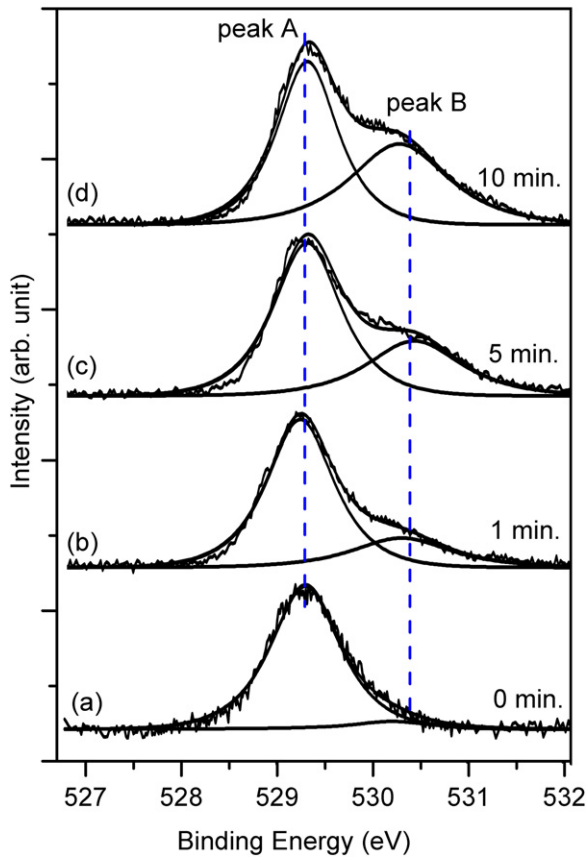


Figure 5. O 1s photoemission spectra of $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ films subjected to Ar^+ sputtering for the indicated periods of time, in which peak A and B correspond to $\text{Ce}^{4+}\text{-O}$ and $\text{Ce}^{3+}\text{-O}$ contributions, respectively.

indication of the fraction of the Ce ions that are in the Ce^{3+} state and thus the relative amounts of oxygen vacancies. As clearly seen from figure 5, the relative area of peak B is very small (about 8.1% as shown in figure 5(a)) for the as deposited $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ films, and evolves to about 55.2% for the films that have undergone 10 min of Ar^+ sputtering, as shown in figure 5(d), indicating increase of the fraction of Ce^{3+} ions as well as V_O density introduced by Ar^+ sputtering.

The effect of Ar^+ sputtering on the introduction of additional V_O was further investigated by Raman spectroscopy. Fluorite structure metal dioxides such as CeO_2 have only a single allowed Raman mode, which has F 2g symmetry with a symmetric breathing mode of the O atoms around each cation. The mode frequency is nearly independent of the cation mass since only the O atoms move in this mode. For fluorite CeO_2 this frequency is 465 cm^{-1} . Figure 6 shows the Raman spectra obtained from the as deposited films and the films exposed to Ar^+ sputtering. It can be seen that there are small systematic shifts of the F 2g mode to lower frequency and its FWHM becomes wider with the increasing of the period of Ar^+ sputtering time. In addition there also emerges a weak shoulder on the high frequency side of the spectra which evolves into a broad peak at 570 cm^{-1} for Ar^+ films sputtered for longer. The negative shift of the mode frequency, as well as the emergence of the peak at 570 cm^{-1} , according to McBride

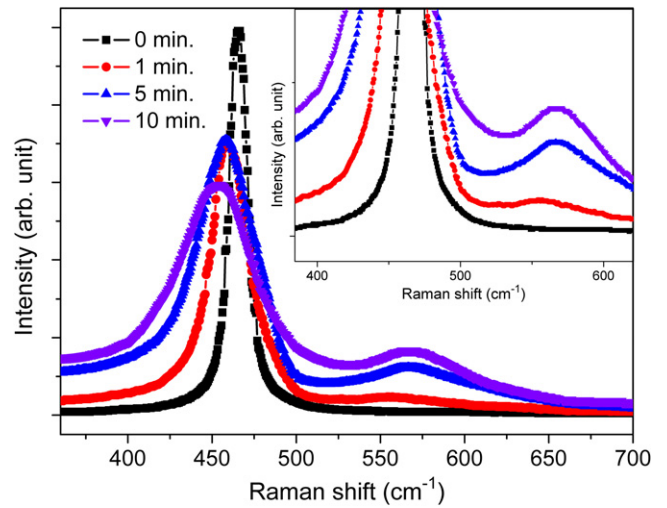


Figure 6. Raman spectra of $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ films subjected to Ar^+ sputtering for the indicated periods of time. The inset shows the Raman spectra with a scale more suitable for observing the small Raman shift and the broad low intensity peak at 570 cm^{-1} .

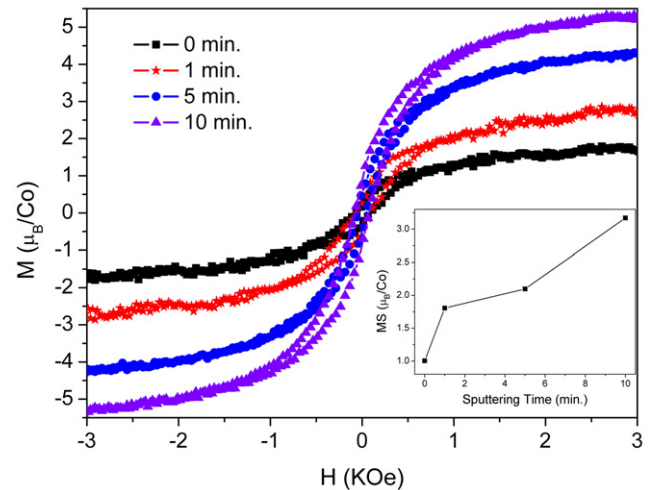


Figure 7. RT $M\text{-}H$ loops of $\text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta}$ films subjected to Ar^+ sputtering for the indicated periods of time. The inset shows the detailed M_S dependence on the Ar^+ sputtering time.

et al [25], can be identified as arising from V_O which was partly introduced by Ar^+ sputtering in our experiment. We can thus conclude that there is an increase of V_O density in the films obtained with longer Ar^+ sputtering times.

Figure 7 shows the RT magnetization versus field ($M\text{-}H$) loops of Co doped films subjected to Ar^+ sputtering for different times. The inset shows the summarized M_S dependence on the Ar^+ sputtering time. It is found that Ar^+ sputtering has an obvious effect on the FM of Co doped CeO_2 films, i.e., the observed M_S is enhanced with increase of the sputtering time. According to the XPS and Raman spectra referred to above, the enhancement of the FM can be firmly attributed to the additional V_O which was introduced by Ar^+ sputtering. This result provides a straightforward confirmation for the FCE mechanism proposed recently, which relates to

FM origination in insulating DMO. As indicated by the FCE mechanism, it is the V_O or so-called F-centers which provide the coupling centers for Co^{2+} ions. With the increase of V_O density, more Co^{2+} ions would be incorporated into the ferromagnetic coupling via the delocalized electrons trapped in V_O , leading to the enhanced FM which is observed in Ar^+ sputtered $Ce_{0.97}Co_{0.03}O_{2-\delta}$ films in our experiment.

4. Conclusion

In summary, RT FM has been observed in $Ce_{0.97}Co_{0.03}O_{2-\delta}$ films prepared on $Al_2O_3(0001)$ substrates by long range magnetron sputtering. Aiming at an investigation of the V_O mediated FM mechanism, the Ar^+ sputtering method was used to investigate as deposited films and the effect on its FM was investigated also. The XPS and Raman results indicate that Ar^+ sputtering introduces additional V_O into the as deposited films, which leads to an enhanced FM. The experimental results provide direct evidence of V_O enhanced FM, thus providing a straightforward confirmation of the FCE mechanism relating to the FM origination in insulating DMO, such as Co doped CeO_2 compounds.

Acknowledgments

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