Ferromagnetism in sputtered Co doped CeO₂ thin film on Al₂O₃ (0001) substrate

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Abstract. Diluted Co doped CeO₂ films with the stoichiometry of Ce₀.₉₇Co₀.₃O₂₋δ have been prepared via long range magnetron sputtering under varied O₂ flux. Films were thoroughly characterized using X-ray diffraction (XRD), atomic force microscopy (AFM), optical transmission spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and magnetic measurements. The results indicate all film are ferromagnetism (FM) at room temperature, of which the saturated magnetization moments (Mₛ) are changed according to the O₂ pressure adopted in deposition. This phenomenon is well consistent with the oxygen vacancy (V₀, or so called F-center) mediated FM mechanism which was recently proposed to interpret FM found in insulating diluted magnetic oxides (DMOs) system. For further exploration of the oxygen dependent of the Mₛ, oxygen non-stoichiometry was characterized by XPS. It shows that film deposited at lower O₂ pressure contains less oxygen weight or more oxygen vacancies, lead to an enhanced Mₛ and vice versa.

1. Introduction
Diluted magnetic semiconductors, as recently developed materials with novel functionality, are very promisingly to realize the spin injection into normal semiconductors, to facilitate new emerging spintronic devices. A great deal of investigations have been carried out on the exploration of transitional metals (TMs)-doped semiconductors or insulators such as ZnO[1, 2], TiO₂[3], SnO₂[4], HfO₂[5]. In special, the recently developed diluted magnetic oxide of Co doped CeO₂ has gained much attention. Co doped ceria either in bulk[6] or film[7-9] forms are reported with intrinsic FM at the temperature well above room temperature. The high Tc-FM obtained in these TMs-doped insulating oxides such as doped CeO₂ or HfO₂ refers to an V₀ mediated FM mechanism which is comparing with the carrier induced FM mechanism usually used to explain the FM in doped semiconductors. Besides, CeO₂ itself is a promising candidate to be used in silicon-on-insulator structure for high speed devices. Successful fabrication of FM Co doped CeO₂ films bring a potential usage for this material in spintronic devices, e. g., being used in spin transistor[10, 11] or other proposed spin filter devices[12, 13] In proposed spintronic devices, Co doped CeO₂ film can act as a spin filter layer, via which much...
higher degree of spin polarization of injected carriers can be achieved by the tunneling of non-polarized carriers through this ferromagnetic insulator layer.

In this article Co doped CeO$_2$ thin films with the stoichiometry of Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ were deposited on Al$_2$O$_3$(0001) substrate under varied O$_2$ flux. With the characterization of the structure and magnetic properties, results indicate that all the as deposited films are ferromagnetism (FM) at room temperature, of which the saturated magnetization moments ($M_S$) are changed according to the O$_2$ flux adopted in deposition. This phenomenon is well consistent with the F-center mediated FM mechanism which was recently proposed to interpret FM found in insulating DMOs system.

2. Experiment details
Co doped CeO$_2$ films with the stoichiometry of Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ were deposited on Al$_2$O$_3$ (0001) substrates by long range magnetron sputtering method. The target was sputtered in a background vacuum of 10$^{-6}$Pa, on to Al$_2$O$_3$ (0001) substrates which were preheated to 723K. During the deposition process, the target-substrate distance (TSD) was kept at about 40 centimeters. This long distance, which is much larger than the usual TSD adopted in magnetron sputtering, makes the growth rate slow enough thus leading to the as deposited film in high quality. In fact, films about 1µm in thickness were obtained by sputtering for 20 hours with the power of 60W. In order to change the oxygen content in the as deposited films, different O$_2$ flux was injected into the chamber during films deposition. The microstructure was thoroughly characterized using XRD (Cu K$_\alpha$ source) and AFM. Light transmittance was also measured by optical transmission spectroscopy. The magnetic properties were measured using Vibrating Sample Magnetometer (VSM, Model BHV-525) with a resolution of 1×10$^{-6}$ emu. XPS measurement was carried out using Al K$_\alpha$ source. The obtained spectra were all calibrated with C1s (E$_{b}$=284.8 eV).

3. Result and discussion
Figure 1 (a) shows the typical XRD pattern of the film deposited under 20sccm O$_2$. Other samples deposited with smaller O$_2$ flux have the similar XRD patterns. As can be seen that films deposited with varied O$_2$ flux are well crystallized with a preferential orientation along CeO$_2$(001) direction, except very small amount of (111) orientation. There is no any evidence of other impurity phase rather than CeO$_2$ fluorite structure. The good crystallization can also be found in Figure 1 (b) of AFM characterization. It shows a typical micromorphology of the film deposited under 20sccm O$_2$ which demonstrates a good crystalline quality. We find an O$_2$ flux dependency for crystal size, i.e., grain size grows larger with the decrease of O$_2$ pressure, but not given here.

![Figure 1](image)

(a)

(b)

Figure 1. (a) Typical XRD pattern for the as deposited Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ films on Al$_2$O$_3$(0001) substrates under 20sccm O$_2$ flux. The inset shows a scaled-up part to show the low intensity of CeO$_2$(111) orientation. (b) Typical AFM image for the Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ film deposited under 20sccm O$_2$ flux.
To further validate the phase purity of the as deposited Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ films, XPS characterization of Co-2p spectrum has been carried out. As shown in figure 2, the peaks for Co 2p$_{3/2}$ and 2p$_{1/2}$ and their shakeups are fitted using 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[14], excludes the possibility of the Co cluster formation. Besides, two strong shake-up satellites as labeled in figure 2 emerge at high energy level of Co 2p$_{3/2}$ and 2p$_{1/2}$, which affords a typical evidence for bivalent cobalt ions exist in the as deposited Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ films.

The wavelength dependence of optical transmittance spectra of the films prepared under different O$_2$ flux are shown in figure 3. The optical transmittance is in direct ratio with the adopted O$_2$ flux, i.e., it increases from 64% to 90% (at=600 nm) with the increase of O$_2$ flux from 0 to 20 sccm. The low transmittance at low oxygen pressures is due to non-stoichiometric of oxygen atom in Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ films. Non-stoichiometry of oxygen atom would cause many defects, which are quite prone to oxygen vacancies in CeO$_2$, while it still retains its fluorite crystal structure over a wide range of non-stoichiometric compositions through the inclusion of oxygen vacancies.[15-17]

Figure 4 shows magnetization versus fields (M-H) loops of the as deposited films with varied O$_2$ flux during sputtering process. It indicates that all the as deposited films are ferromagnetic with different $M_S$, which is essentially influenced by the value of O$_2$ flux. Films deposited in lower O$_2$ flux obtain the largest $M_S$ which decrease consistently with the increase of O$_2$ flux.
The dependence of \( M_z \) on adopted oxygen flux is intimate with the oxygen non-stoichiometry in as deposited \( \text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta} \) films. Here XPS characterizations of Ce 3d and O 1s are employed to quantify oxygen non-stoichiometry as well as to characterize oxygen vacancies. The standard analysis techniques are applied here to the data for each of the core levels (Ce 3d, O 1s).

The change of oxygen non-stoichiometry is firstly studied by analyzing Ce 3d spectrum. As well known that with oxygen deficiency, \( \text{Ce}^{4+} \) would be reduced to \( \text{Ce}^{3+} \) in \( \text{CeO}_2 \) while still retain 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 oxygen vacancies in \( \text{CeO}_2 \) comparatively by comparing of \( \text{Ce}^{3+} \) relative weight. We firstly figure out the peak positions corresponding to \( \text{Ce}^{3+} \), then by comparing the variation of the spectrum in these positions to qualitatively measure \( \text{Ce}^{3+} \) content. Figure 5 presents the changes in the Ce 3d XPS spectra of \( \text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta} \) films deposited under varied \( \text{O}_2 \) flux. As well known that \( \text{CeO}_2 \) has a complex Ce core photoelectron structure. Ce 3d core level spectrum contains about ten peaks, four attributed to the Ce 3+ and six due to the Ce 4+ valence state. The peak assignments are discussed in detail in the literature.[18, 19] But Ce 3d spectra itself is not the focus here. For the sake of simple, we only pay attentions on the main peaks which could be obviously attributed to Ce 4+ or Ce 3+ valence state. As shown in figure 5, the peaks corresponding to \( \text{Ce}^{4+} \) 3d\( \epsilon/2 \) and \( \text{Ce}^{4+} \) 3d\( \epsilon/2 \) are designated at binding energies of 916.9 eV and 898.3 eV, and those of \( \text{Ce}^{3+} \) 3d\( \epsilon/2 \) and \( \text{Ce}^{3+} \) 3d\( \epsilon/2 \) are indicated at 903.9 and 886.4 eV, respectively. It can be seen that the intensity of Ce 3+ 3d peaks in films apparently increases with decreasing of the adopted \( \text{O}_2 \) flux, implying the increased amount of oxygen vacancies with the reduction of ceria.

![Figure 5. Ce 3d photoemission spectra of Ce\(_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta} \) films deposited under varied oxygen flux as indicated in the figure, in which the position corresponding to Ce\(^{3+}\) and Ce\(^{4+}\) are labeled, respectively.](image)

The oxygen peaks are used as another source of information about the cerium oxidation state here. In \( \text{Ce}_{0.97}\text{Co}_{0.03}\text{O}_{2-\delta} \), O 1s spectrum is 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 \( \text{Co}^{2+}\text{-O} \) bond should be at higher binding energy than that of the O 1s peak from Ce-O bond, as Co has a higher electronegativity (1.88 on the Pauling scale) than Ce (1.12). One would expect that 1s electrons in oxygen attached to cerium atoms in the (+3) oxidation state would be more tightly bound than for cerium in the (+4) state. But the spectrum can be well fitted by two Gaussian peaks as shown in figure 6. According to the above analysis, peak A and B are from Ce\(^{3+}\)-O and Ce\(^{3+}\)-O species, respectively. The individual peak corresponding to \( \text{Co}^{2+}\text{-O} \) bond is covered up as there is very low Co concentration in the as deposited films. Examining the relative areas of peaks A and B gives an indication of the fraction of the Ce ions that are in the Ce\(^{3+}\) state and thus the relative amount of oxygen vacancies. As clearly seen from figure 6, the relative area of peak B reduces rapidly for films deposited with higher \( \text{O}_2 \) flux, indicating the reduction of the fraction of Ce\(^{3+}\) ions as well as oxygen vacancies. It should be stressed here that absorbed oxygen always come into being on the surface of some oxides such as CeO\(_2\), leading to a confusion of the O XPS result. But it is more or less the reflection of the oxygen content variation in different samples, by the obvious dependence between peak B and \( \text{O}_2 \) flux. Angle dependent XPS could be used for more detailed investigations, and relevant work are in progress.
According to the XPS&VSM results, there are more Ce$^{3+}$ ions or oxygen vacancies in films deposited with lower O$_2$ flux, which lead to a larger $M_S$ and vice versa. As we know that, Ce$^{3+}$ with the electronic structure of [Xe]4f$^1$ is paramagnetic thus has no contribution to the observed FM in Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$, which has been proved by the electronic paramagnetic resonance measurement of reduced pure CeO$_2$[20]. But alternatively, the $V_O$ dependent of $M_S$ is just very consistent with the FCE mechanism recently proposed. According to the FCE mechanism, it is the $F$-centers which provide the coupling centers for Co$^{2+}$ ions. In our experiments, there are more oxygen vacancies in lower O$_2$ flux-deposited Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ films. 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 observed in low O$_2$ pressure-deposited Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ films.

4. Conclusion
In summary, preferential oriented Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ films were deposited on Al$_2$O$_3$ (0001) under varied O$_2$ flux. All the as deposited films are FM at room temperature, and the $M_S$ is in inverse ratio with O$_2$ flux. The results are well consistent with FCE mechanism. Aiming at the FM origination mechanism in diluted magnetic oxide, which is still in strong debate recently, oxygen non-stoichiometry as a function of the adopted O$_2$ flux has been investigated by Ce 3d and O 1s XPS spectra. It indicates an $V_O$-related FM, i.e., there are more oxygen vacancies in lower O$_2$ flux-deposited Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ films, which leads to the highly enhanced $M_S$. The result gives direct proof for the $V_O$ or $F$-center mediated FM in Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ compounds, and thus very helpful in understanding the mechanism of the FM origination in many TMs-doped insulating DMOs.

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