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Structural properties of Fe doped TiO_2 films on $LaAlO_3$ and Si substrates

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ABSTRACT

We have prepared 4 at.% Fe doped TiO_2 thin films on LAO (001) and Si (111) substrates by pulsed laser deposition. X-ray diffraction (XRD) studies suggest different structural properties of the films on the different substrates. Raman measurements corroborate the XRD findings. The thicknesses of the films are also different on the two substrates, suggesting different nucleation process on the two substrates. Interestingly on both the substrates, Fe is not in metal clusters, suggesting their possible incorporation in TiO_2 matrix.

Keywords: Thin film; doped TiO_2; pulsed laser deposition; X-ray diffraction; DMS.
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Introduction

The realization of materials that combine semiconducting behavior with robust magnetism has been attracting materials physicist as one can control electrical properties using magnetic field or vice versa. The basic idea behind it is the spin polarized transport in such materials for their possible exploration in spintronics devices. Spintronics is a new and more powerful branch of electronics in which the spin property of electrons, in addition to their charge, is utilized to achieve greater efficiency and functionality. Manipulating an electron's magnetic state in a semiconductor device is the key to successful spintronics, and the simplest way to do that is by using a semiconductor material such as gallium arsenide (GaAs, ZnO, TiO_2 etc.), which incorporates magnetic elements like manganese (Mn, Co, Fe having some net spin) [**1-5**]. The result is a new class of materials now known as diluted magnetic semiconductors (DMSs). Mn-doped GaAs is an example of the early and ongoing efforts with diluted magnetic impurities in III-V semiconductors which produced successful ferromagnetic semiconductors at low temperature [**1**]. The search for ferromagnetism in a semiconductor at room temperature was accelerated with the predictions of Dietl *et al.* who performed an exhaustive theoretical study of potential candidate materials in 2000 [**2**]. They notably predicted room temperature ferromagnetism for 5% Mn doped ZnO (T_c above 300K). This prediction opened a way to achieve room temperature operation with dilute magnetic oxides such as SnO_2, TiO_2,

MoO_3, $La_{0.5}Sr_{0.5}TiO_3$ etc. [**3-5**]. However origin of ferromagnetism in these systems remains controversy.

In order to understand the nature of DMS, to recognize and control the foundation of ferromagnetism, it is important to address about dependence of cluster configuration on growth conditions, effect of oxygen content, the valence state of cation or the magnetic impurity, chemical compatibility of the dopant magnetic impurity with the host matrix, effect of carrier concentration on magnetic as well as the electrical properties. In the present manuscript we show the effect of substrate on the structural and electrical properties of Fe doped TiO_2 films.

Experimental

The targets used for the deposition were sintered pellets of $Ti_{0.96}Fe_{0.04}O_2$. The pellets were prepared by solid-state reaction route. 200-nm-thick films were grown by the pulsed laser deposition technique using KrF laser (248 nm) on (001) $LaAlO_3$ (LAO) and (111) Si substrates heated at 600 °C. Before the depsoition substrates were chemically cleaned. The laser repetition rate and energy density at the target surface for the deposition were kept at 10 Hz and 2 J/cm^2 respectively. Deposition was carried out under the oxygen partial pressure of 1x10^{-4} Torr for 20 minutes. After the deposition, substrates were cooled down to room temperature in the same oxygen partial pressure as used during the deposition. Thickness of the films was determined by using tele-step method and it turns out that while film grown LAO substrate has thickness ~180 nm, the film grown on Si substrate has thickness only ~100 nm. This suggests that sticking coefficient and nucleation of TiO2 film is different on these substrates. Structural properties of these films were studied with X-ray diffraction (XRD) and Raman spectroscopy measurements. We chose LAO substrate to grow Fe doped TiO_2 films since lattice parameter of anatase TiO_2 (0.3785 nm) is very close to that of $LaAlO_3$ (0.3788 nm), leading to small lattice mismatch (0.079%) with the substrate. We X-ray photoelectron spectroscopy (XPS) was performed using Al-K_α (λ = 0.834 nm) lab-source to reveal the valence state of Ti and Fe in the films.

Results and discussion

We perform the XRD measurements at high power (4 kW, current 100 mA and voltage 40 kV) of Fe doped TiO_2 thin films and plotted them in log scale as shown in **Fig. 1**. This would help us in detecting the presence of any impurity phase such as Fe clusters, FeO, Fe_2O_3 or Fe_3O_4 phase or co-occurrence of different phases of TiO_2 in these films. From the patterns it is evident that the film on LAO substrates is mostly anatase in nature. However, we also note the that film grown on LAO substrate has other TiO_2 phase like brookite structure also present **Fig. 1(a)**. Interestingly film grown on Si substrate shows only rutile phase, though intensity of the phase is very weak **Fig. 1(b**). This suggests that crystalline property of the film on Si is very weak and that its nucleation on Si substrate is different than on LAO substrate. The prominent anatase phase of Fe doped TiO_2 film on LAO substrate is expected because of the close matching of lattice parameters between the phase and the LAO substrate. Since Si lattice parameter is quite different than TiO_2 lattice parameters, film grown under present condition, nucleates according to the most stable phase of TiO_2. It should be recalled here that mainly TiO_2 is found in three crystalline forms: rutile, anatase and brookite. The bulk TiO_2 is stable in rutile phase at room temperature and anatase phase is not stable. However in the thin film form the phase of TiO_2 can be controlled by a proper choice of the substrate and deposition condition, as has been shown in present case on LAO substrate. We do not detect any Fe based impurity phase in these films. Compositional stoichiometry was confirmed using energy dispersive X-ray spectroscopy. These films show very smooth surface as revealed by scanning electron microscopy, and shown in **Fig. 1**(**c**) for the film on LAO substrate.

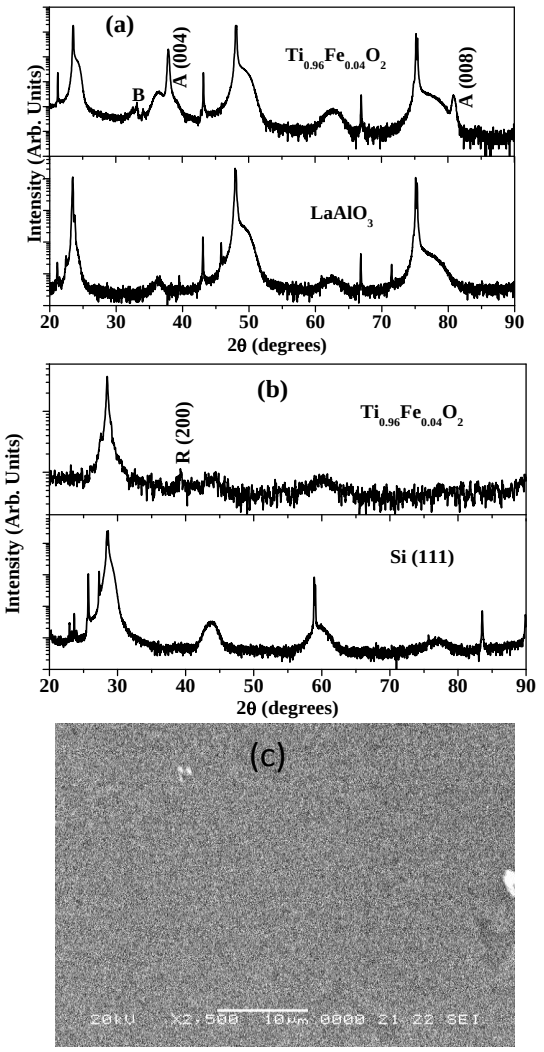

Fig. 1. XRD patterns of 4 at. % Fe doped TiO_2 films on (a) LAO substrate (b) Si substrate; along with xrd patterns of respective substrates. Symbols A, R and B represent anatase, rutile and brookite phases respectively. (c) SEM image of the film on LAO substrate.

We further confirm their structural properties using micro Raman spectroscopy measurements. The Raman spectra 4% Fe doped TiO_2 films grown on LAO and Si substrates are shown in **Fig. 2** (**a**) and (**b**) respectively. We observe Raman modes at 399 cm^{-1} and 517 cm^{-1} corresponding to Anatase phase on LAO substrate, whereas, film on Si substrate show Raman mode at 143 cm^{-1} corresponding to rutile phase [**6**]. Raman spectra corroborates with the findings of XRD results that film grown on LAO substrate has prominent anatase TiO_2 phase, whereas the film grown on Si substrate has rutile phase.

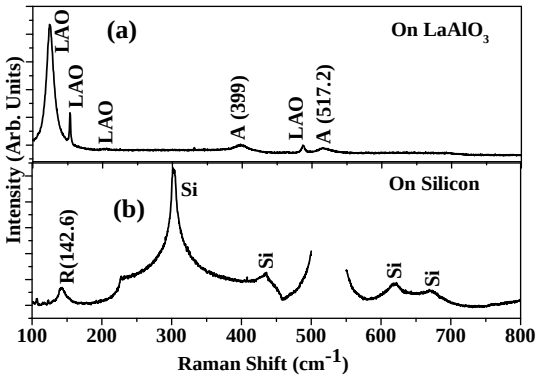

Fig. 2. Raman spectra of Fe doped TiO_2 films on (a) LAO substrate (b) On Silicon substrate. Symbols A and R represent anatase and rutile phases, respectively.

To investigate the chemical state and surface composition of elements present in the samples we have performed XPS measurements of these films. XPS spectra were similar for both the films. **Fig. 3**(**a**) shows the XPS survey spectra of the 4%Fe doped TiO_2 films grown on LAO substrate. The survey spectrum clearly shows strong features due to Ti and O present in the samples. Because of very low doping, feature due to Fe has very weak signal in the wide scan. No other impurity is present except signal from the C-1s. All peaks present in the spectrum correspond to different elements, are indicated in the fig. To further analyze core level spectra of the samples, we have performed the detailed scan of Ti-2p and O-1s core levels along with Fe-2p core level.

The oxygen 1s core level spectra recorded for the sample is shown in inset of **Fig. 3**(**a**). It consists of two peaks: one is at position 530.6 eV corresponding to 1s which makes bond with Ti for TiO_2 and the other is at 533.2 eV which corresponds to nascent oxygen present on the sample surface. The intensity of feature due to nascent oxygen is higher since the presented spectrum is of as grown film, which is not sputtered.

In **Fig. 3**(**b**) we show the Ti-2p core level spectra. The spectra clearly show $Ti_2p_{3/2}$ and $Ti_2p_{1/2}$ peaks at 458.22 eV and 463.88 eV (at the reported difference of 5.7 eV) and exactly matches to the peak positions respectively. It confirms the presence of TiO_2. From the area under the $Ti2p_{3/2}$ peak and O1s peak, we have also calculated the stoichiometry of the sample on the surface and found to be same as expected.

Finally, to investigate the ionic state of Fe in the films we performed detailed scan of Fe2p core level spectra, as shown in **Fig. 3**(**c**). From the Fe2p spectra we observe that the Fe2p1/2 and Fe2p3/2 peaks are situated at around 722.8 eV and 709.2 eV respectively. From handbook of XPS, it is known that the peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ for Fe metal is located at 706.75 eV and 719.95 eV, for Fe^{2+} states at 709.3 and 722.3 eV and for Fe^{3+} in Fe_2O_3 at 710.70 eV and 724.30 eV, respectively [**7, 8**]. We find that in our film Fe 2p core level spectra match well with Fe^{2+} state. However, the peaks are broadened, which could be due to small presence of Fe^{3+} ions also. The observation confirms that Fe is not present in metal or cluster form in TiO_2 matrix.

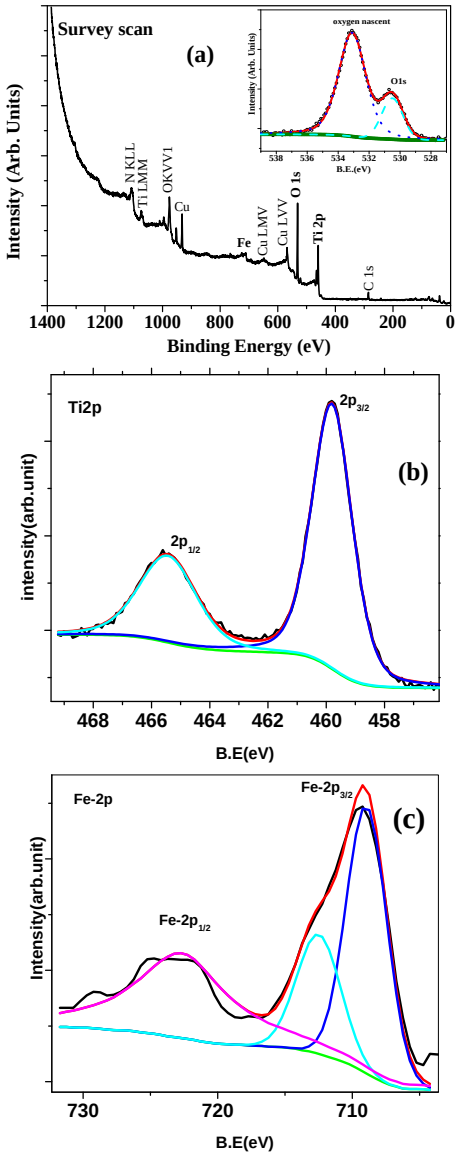

Fig. 3. (a) Survey scan spectra of Fe doped TiO_2 film on LAO substrate showing different elements present in the film, inset shows the O-1s core level spectra; (b) and (c) show the Ti-2p and Fe-2p core level spectra respectively.

Conclusion

Our results emphasize that Fe doped TiO_2 films grown on LAO and Si substrtates show different TiO_2 phase structure. While film on LAO is prominently anatase, film on Si is rutile in nature. Raman spectra confirm the XRD findings. Fe is present in ionic state in TiO_2 films on LAO and Si substrates, which rules out the possibility of metal cluster formation.

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