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A. Roy Barman, A. Annadi, K. Gopinadhan, W. M. Lú, Ariando, S. Dhar, and T. Venkatesan

Interplay between carrier and cationic defect concentration in ferromagnetism of anatase $Ti_{1-x}Ta_xO_2$ thin films

A. Roy Barman,[1,2] A. Annadi,[1,2] K. Gopinadhan,[1,3] W. M. Lú,[1,3] Ariando,[1,2] S. Dhar,[1,3] and T. Venkatesan[1,2,3]
[1]*NUSNNI-NanoCore, National University of Singapore, Singapore 117576 Singapore*
[2]*Department of Physics, National University of Singapore, Singapore 117542 Singapore*
[3]*Department of Electrical and Computer Engineering, National University of Singapore, Singapore 117576 Singapore*

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Thin films of Ta incorporated TiO_2 grown by pulsed laser deposition under specific growth conditions show room temperature ferromagnetism. Ta introduces carriers and concomitantly cationic defects, the combination of which leads to ferromagnetism. In this paper, we report on the dependence of the carrier and cationic defect density (compensation) on various parameters such as oxygen growth pressure, temperature and Ta concentration. Most likely, the Ti vacancies act as magnetic centers and the free electrons help with the exchange leading to ferromagnetism via Ruderman-Kittel-Kasuya-Yosida mechanism. [http://dx.doi.org/10.1063/1.3690113]

Conventional electronics have made use of only the charge of electrons in semiconductors for various integrated circuits and devices. With the interest swelling in the field of spintronic, magneto-optic and opto-electronic devices more researchers are exploring the possibility of utilizing the spin degree of freedom for electrons by inducing magnetism in non-magnetic semiconductors.[1–5] Probably the most common route to achieve magnetism in non-magnetic semiconductors has been doping of the semiconductors with magnetic elements leading to dilute magnetic semiconductors (DMS).[6–8] Currently the most successful and reproducible DMS system has been Mn-doped GaAs.[9–11] However, with the Curie temperature for the system being well below room temperature (RT), its use in practical devices is limited.

On the other hand, sophisticated growth techniques have significantly advanced the field of metal oxide thin films, which due to their versatility and multifunctionality have gained considerable importance among material scientists.[8] There has been a lot of activity over the last decade in dilute magnetic doping of oxide semiconductors, to produce DMS oxides (DMSO). Being substantially different from conventional semiconductors, oxides have already proved to be a very rich system for studying various dopant effects. Historically, Matsumoto *et al.*[12] were the first to observe ferromagnetism in Co doped TiO_2. Ever since then, systems such as TiO_2 and ZnO have been extensively studied for DMSO with a wide range of metallic and non-metallic dopants. In spite of all such developments the field of DMSO has been plagued with controversies ever since its inception. This is mainly due to the many inconsistent results in this field related to secondary phase formation, impurity effects and solubility/clustering/segregation of the magnetic impurity in the host oxide.[13]

Another possible route to DMSO is via defect engineering.[8] In this approach, cationic or anionic vacancies are created intentionally in the host matrix. These vacancies act as magnetic centers. It has been predicted theoretically by Elfimov *et al.*[14,15] that cationic vacancy in non-magnetic CaO can lead to local magnetic moments. Osorio-Guillén *et al.*[15] had calculated the formation energies of such defects to be substantially lower in the presence of electron or hole doping in the host crystal of a binary oxide system.

Recently, Zhang *et al.*[9] had reported Kondo scattering in Nb incorporated TiO_2. This was the first experimental observation of local magnetic moments formed due to Ti vacancies (V_{Ti}) which were found to increase with Nb incorporation. Finally, Rusydi *et al.*[10] reported ferromagnetism in Ta incorporated TiO_2 using various sophisticated, element specific techniques like soft X-Ray magnetic circular dichroism (SXMCD) and optical magnetic circular dichroism (OMCD) apart from SQUID magnetometry. The magnetism in this system has been argued to arise due to the local magnetic moments of the V_{Ti} which couple through the free electrons via Ruderman-Kittel-Kasuya-Yosida (RKKY)-type exchange interaction. Though, traditionally researchers have referred to "doping" oxides with various elements, the authors of this paper have proved[11] that Ta incorporation (>1%) in TiO_2 leads to the formation of a new alloy with a totally distinct band structure as compared to "undoped" TiO_2. This is expected, since without a drastic change in the electronic properties of $Ti_{1-x}Ta_xO_2$, it is hard to explain the ferromagnetism. In this paper, we first discuss the sample preparation and the consistency of ferromagnetism in the $Ti_{1-x}Ta_xO_2$ thin films. We show the systematic variation of the magnetization with the deposition parameters. We also elucidate the effect and/or role of Ta in inducing V_{Ti} in the $Ti_{1-x}Ta_xO_2$ thin films and introducing the free carriers necessary for the RKKY interaction.

Thin films of $Ti_{1-x}Ta_xO_2$ ($x = 0.000 - 0.08$) were grown epitaxially on LAO substrates using the pulsed laser deposition (PLD) technique using a Lambda Physik KrF excimer laser with wavelength 248 nm and pulse width of approximately 15 ns. The laser energy density was maintained at $2J/cm^2$ with pulse frequency at 5 Hz for all the depositions. The duration of the deposition was optimized to get films of about 30 nm thicknesses. The targets used for the depositions were prepared from high purity (99.999%) TiO_2 and Ta_2O_5 powders. The powders were carefully weighed, mixed and ground for several hours before being sintered at 1000°C for 20 hours. Next, the powders were pressed into pellets and calcinated at 1100°C for 24 hours. The growth temperature and the oxygen partial pressure were varied between 500-700°C and from $1x10^{-3}$ down to $1x10^{-5}$ Torr, respectively.

The structural phases of all the films were characterized by Bruker D8 X-Ray Diffractometer. All the films prepared at or above 600°C were found to be in the perfect anatase form.[16] The crystal quality of the films, the exact Ta concentrations and their Ta substitutionality at the Ti lattice sites were measured quantitatively using Rutherford backscattering (RBS)-Ion channeling spectroscopy. The detailed analysis of RBS spectroscopy on the magnetic $Ti_{1-x}Ta_xO_2$ thin films will be discussed elsewhere. Also an extremely thorough and detailed scrutiny, involving RBS spectroscopy, Proton Induced X-Ray Emission (PIXE), X-Ray Absorption Spectroscopy (XAS) and Secondary Ion Mass Spectroscopy (SIMS) has been done on the magnetic $Ti_{1-x}Ta_xO_2$ thin films and the PLD targets used to rule out any impurity artifacts issues.[17]

To optimize the magnetization induced by Ta in TiO_2, we studied the film growth under varying oxygen partial pressure, deposition temperature and Ta concentration. Magnetization measurements were done by Quantum Design SQUID system. We obtained electrical transport data to understand the effect of Ta incorporation on the magnetization of $Ti_{1-x}Ta_xO_2$ thin films, with Hall measurements done using a Van der Pauw geometry. All the TiO_2 films incorporated with Ta showed metallic behavior.

Oxygen partial pressure is an extremely important deposition parameter for any oxide thin film grown by PLD. In Fig. 1(a), saturation magnetization and the carrier density of the samples are plotted as a function of oxygen partial pressure keeping the deposition temperature fixed at 600°C. It is seen that both the magnetization and the electron density for the films are highest at $1x10^{-5}$ Torr and gradually fall off as the pressure is increased. Structurally, $Ti_{1-x}Ta_xO_2$ thin films grown below $1x10^{-5}$ Torr will produce rutile films. The electron mobility of $Ti_{1-x}Ta_xO_2$ thin films in rutile phase is orders of magnitude lower than the anatase films.[18] As such, it is understandable that for the rutile films, RKKY exchange mechanism is almost nullified and no perceptible magnetism is seen. At higher oxygen partial pressure ($1x10^{-4}$ Torr), the thin films have less oxygen vacancies and the carrier density is measured to be lower than for the films grown at lower oxygen partial pressure ($1x10^{-5}$ Torr). Since the films grown at $1x10^{-5}$ Torr oxygen partial pressures have higher number of free carriers, the RKKY mechanism is enhanced. This explains the higher saturation magnetization for films grown at $1x10^{-5}$ Torr oxygen partial pressure.

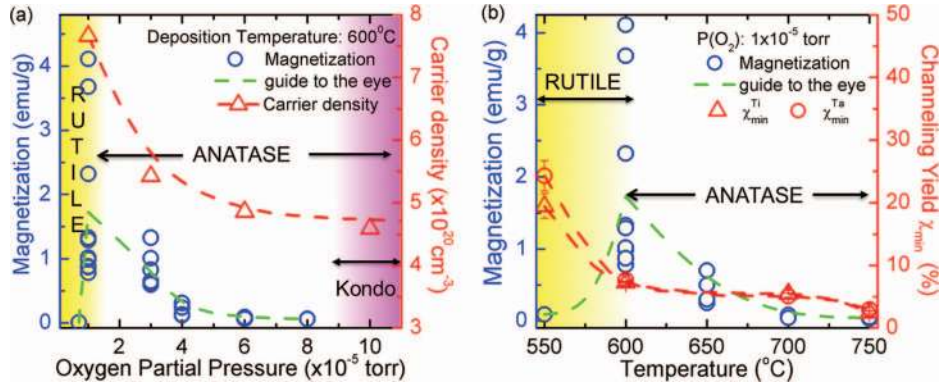

FIG. 1. (a) Variation of magnetization as a function of oxygen partial pressure (left ordinate). Blue solid circles represent magnetization for multiple samples while the dotted line represents the average value; Variation of carrier density as a function of oxygen partial pressure (right ordinate). (b) Variation of magnetization as a function of deposition temperature (left ordinate). Blue solid circles represent magnetization for multiple samples while the dotted line represents the average value; Decrease of minimum channeling yield for Ti and Ta with increasing deposition temperature (right ordinate).

Similarly, Fig. 1(b) shows the saturation magnetization of the $Ti_{1-x}Ta_xO_2$ thin films as a function of deposition temperature. The magnetization value peaks at 600°C and decreases considerably as the temperature is increased to 750°C. For temperatures below 600°C, the formation of rutile phase inhibits magnetism. RBS-Ion channeling experiments show that both the Ti and the Ta minimum yields decrease with increasing deposition temperature of the films. This clearly tells us that films grown at higher temperatures have better crystallinity as compared to those grown at lower temperatures. This may be annealing out a lot of the defect centers, which provide the magnetic moments necessary for the ferromagnetism in the $Ti_{1-x}Ta_xO_2$ thin films. Here the role of Ti^{3+} becomes very important. At higher temperature it is possible that more Ti^{3+} is produced which may work against FM due to a possible antiferromagnetic alignment.[17] XPS measurements as function of temperature may be quite important to shed more light on this.

Having discussed the importance of deposition parameters on the magnetization of $Ti_{1-x}Ta_xO_2$ thin films, we move on to explain the important role played by the Ta incorporation in TiO_2 crystal. As mentioned above, it has been calculated by theorists that, Ta^{5+} in TiO_2, being an electron donor reduces the formation energies of such defects in the crystal which act as electron acceptors (V_{Ti}, Ti^{3+} or Oxygen interstitials).[19–21] As such, on one hand the Ta incorporation favors magnetism by inducing defect centers with magnetic moments while on the other hand, it hinders the same by reducing the number of free carriers required for the RKKY mechanism. Hence, there should be an optimum condition for Ta incorporation at which we would have enough defect centers and charge carriers at the same time. Highest magnetization should be observed when such a balance is struck. This is experimentally observed as shown in Fig. 2. Saturation magnetization is highest for the samples with Ta incorporation around 6%. It is also interesting to note that the carrier density seems to scale with the measured magnetization.

To realize the maximum possible magnetization in this system we repeated our deposition at the optimized growth condition. Fig. 3(a) shows the magnetization values for ten such samples. The range of the magnetization obtained varies from 0.8 emu/g to 4.11 emu/g. Fig. 3(b) shows a typical hysteresis loop for one of the samples. The coercivities for the films are around 70 Oe and the average magnetization is 1.7 emu/g.

Fig. 4 shows the carrier density of the thin films as a function of the Ta concentration. Though the increase in the carrier density with Ta concentration is quite expected, the nonlinearity of the increase is quite striking. Fig. 4 also shows us that all the carriers from the Ta incorporation in the $Ti_{1-x}Ta_xO_2$ films are not activated. Defects such as V_{Ti} are known as "electron killers" in a system and thus the amount of compensated carriers in a system can be co-related to such defects. Using X-ray absorption measurements it was shown[14] that V_{Ti} are responsible for the ferromagnetism and not Ti^{3+}. As such, it is quite clear from the transport data that the number of compensating

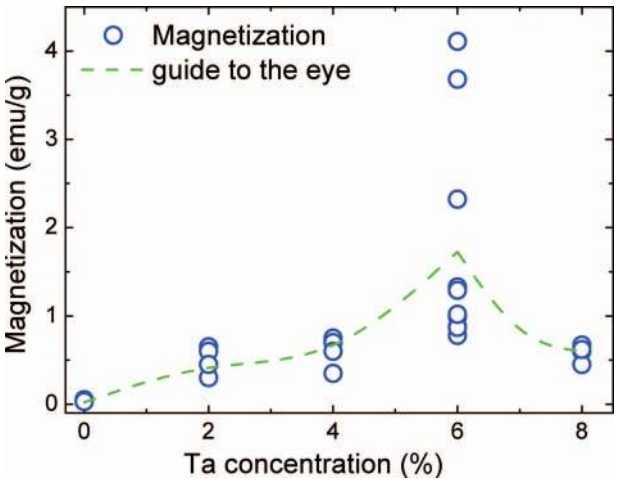

FIG. 2. Variation of magnetization as a function of Ta incorporation in $Ti_{1-x}Ta_xO_2$ thin films. Blue solid circles represent magnetization for multiple samples while the dotted line represents the average value.

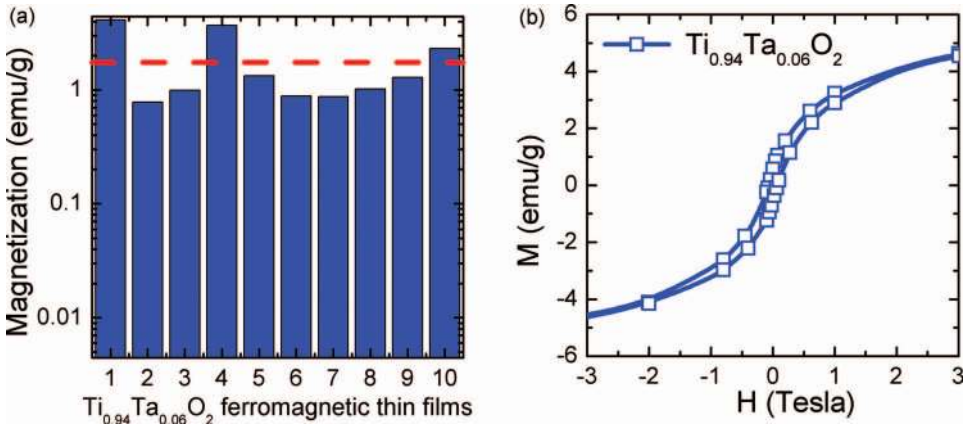

FIG. 3. (a) Statistics for the magnetization data measured on samples grown at 600°C and $1x10^{-5}$ oxygen partial pressure. (b) A hysteresis loop obtained for one such sample.

defects and uncompensated carriers are optimum in the case of the sample which has about 6% Ta incorporation.

Now that V_{Ti} is established as the magnetic entity, we will try to develop a microscopic understanding of the FM. The four unpaired electrons in a Ti vacancy site can align in three possible ways which will yield 4, 2 and 0 μB. Statistically we can assume a value of 2 μB per vacancy which would mean that to get the magnetization value seen, an amount of ~2.5% vacancy would be needed. In addition, to compensate 50% of the free electrons from the Ta, about 0.6% vacancies would be needed. So a total of about 3% V_{Ti} is adequate to explain the saturation magnetization as well as the electron compensation seen which is consistent with the predictions.[15] The average distance between two Ti vacancies is about 3-4 unit cells. Unless the orbital magnetization of the Ti vacancy is extended over at least two unit cells, the direct exchange probability is very low. The fact that the FM is not seen in samples prepared at higher oxygen pressures (but instead Kondo scattering is seen[21]) where the Ti vacancy concentration is higher but the carrier concentration is lower strongly argues in favour of a carrier mediated exchange.[22,23] As the free electron carrier density of the $Ti_{1-x}Ta_xO_2$ (x~0.05) film is about 7.6×10^{20} cm^{-3}, the mechanism of FM is most likely facilitated through itinerant electron-mediated RKKY process. As such, it is necessary to have an optimum number of V_{Ti} and free electrons in our thin films at the same time to achieve

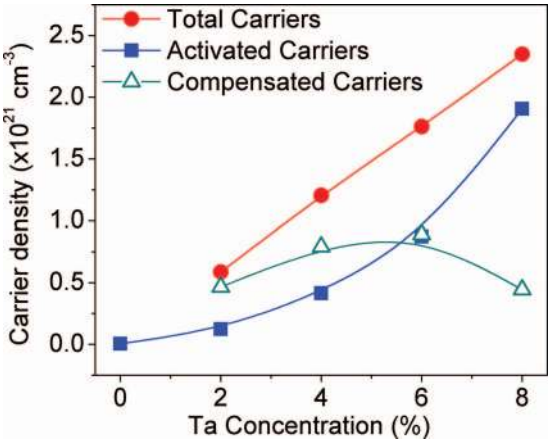

FIG. 4. Variation of the actual activated carrier density as a function of Ta incorporation in $Ti_{1-x}Ta_xO_2$ thin films (blue solid squares). Variation of calculated carrier density as a function of Ta incorporation in $Ti_{1-x}Ta_xO_2$ thin films with 100% carrier activation (red solid circles). Variation of inactivated carrier density as a function of Ta incorporation in $Ti_{1-x}Ta_xO_2$ thin films (green open triangle).

ferromagnetism. This explains why the magnetization of the $Ti_{1-x}Ta_xO_2$ thin films is so sensitive to the PLD growth parameters.

In summary, we have done a detailed analysis of the dependence of defect induced magnetism in $Ti_{1-x}Ta_xO_2$ thin films on Ta concentration and PLD deposition parameters such as the oxygen partial pressure and deposition temperature. Films grown at higher temperatures ($\sim 700^{\circ}$C), show less defects and hence are not suitable for magnetism. Similarly, films grown at high oxygen partial pressure ($\sim 1x10^{-4}$ Torr), have less carrier densities which suppresses the RKKY mediated magnetism. However, for the RKKY process to work, TiO_2 has to be in the anatase phase and this restricts magnetism being seen in films grown at deposition temperatures lower than 600°C and oxygen partial pressure lower than $1x10^{-5}$ Torr. We have also illustrated the role of Ta in inducing magnetism in $Ti_{1-x}Ta_xO_2$ thin films by creating defects (magnetic centers) and by introducing free carriers to help them interact via RKKY mechanism. Ta has the dual role of providing carriers and also enhancing cationic defect formation leading to the defect induced magnetism in the $Ti_{1-x}Ta_xO_2$ thin films.

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