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Review: Ferromagnetism in Undoped ZrO_2 Thin Films

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Abstract: Diluted magnetic oxides have evolved into a popular branch of materials science during the last decade. In the first few years, people attributed the ferromagnetism to the magnetic dopants. However, the observation of ferromagnetism in undoped HfO_2 thin films made it more controversial and promoted extensive research on the ferromagnetism in various undoped oxides. Both of the experimental works and theoretical studies have shown that intrinsic defects in oxide nanomaterials play a crucial role in the origin of such an unexpected ferromagnetism, in spite of some contradicting views which kind of defects is predominant. In the past several years, we have conducted systematic and thorough research on the room temperature ferromagnetism in undoped ZrO_2 thin films, and clarify some physics behind it. We firstly prepared undoped ZrO_2 thin films by different ways, such as Pulsed electron beam deposition, magnetron sputtering, and electron beam evaporation, and successfully obtained ZrO_2 thin films with different crystalline structure, in particular a pure high-temperature stabilized one, by adjusting some preparation parameters during the deposition process or post-annealing treatment. A phase-dependent ferromagnetism was then confirmed to exist in such ZrO_2 thin films. Further, we conducted exhaustive defect analysis and characterization by X-ray photoelectron spectroscopy, photoluminescence spectra, and electron paramagnetic resonance, respectively, and found the oxygen vacancy, specifically the single ionized oxygen vacancy (V_O^+), has a remarkable influence on the enhancement of ferromagnetism. Herein, we will review the work in detail on the phase-dependent and oxygen vacancy-enhanced room temperature ferromagnetism in undoped ZrO_2 thin films.

Keywords: ZrO_2 thin film; ferromagnetism; phase-dependent; oxygen vacancy

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1 Introduction

Ferromagnetic semiconductor or insulator is not new, and has fascinated considerable attention and interest since 1960 s, as it may play an important role in spintronics which has been developing into a most important branch of materials science due to the capability to generate and manipulate the electron spin, another freedom degree besides the electron charge. The hardest challenge here based on the manipulation of spins and charges at the same time is the material should possess both efficient spin-polarized carrier injection and transport[1]. In the early times when ferromagnetic metals were employed as the contacts, the spin injection efficiency was always quite low as a consequence of the large mismatch of density of states (DOS) between the metal and semiconductor[2-5]. That's why developing functional ferromagnetic semiconductor and insulator as spin-injection contacts seems to be quite imperative[6]. However, earliest research showed that the Curie temperatures of most natural magnetic semiconductors were always very low which greatly limited their practical application [7]. Making the semiconductor or insulator ferromagnetic above RT seems to be another challenge. The first theoretical study on room temperature ferromagnetism (RTFM) in semiconductor is conducted by Dietl et al.[8], and indicates the RTFM could be present in 5 at% Mn-doped GaN and ZnO, which triggers a new research hotspot, i.e. diluted magnetic semiconductor (DMS) or diluted magnetic oxide (DMO), and inspires many groups to participate in it, in particular after the subsequent experimental discovery of RTFM within Co-doped TiO_2 films[9]. Since then, RTFM has been observed in various materials, especially in many kinds of wide-band-gap oxides doped by different elements, such as ZnO[10-12], TiO_2[13-15], SnO_2[16-18], In_2O_3[19-21], $SrTiO_3$[22-24], etc., and is attributed to the interaction between the dopant moments and carrier spins of host[25] via different theoretical models such as RKKY[26-27], mean field theory[28-29], or double exchange[30-31], etc. However, someone is being suspicious whether the RTFM in doped DMS or DMO is intrinsic, since it may result from some metallic clusters and secondary phases which are easy to occur in those samples and might be detrimental to the practical application[10].

The first observation of RTFM in HfO_2 thin films without any dopants and impurities by Coey et al.[32-34] indicates that doping might not play any key roles in the

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RTFM of DMS or DMO, and makes the origin and mechanism of RFTM much more controversial, and challenges our understanding of such an unexpected d^0 magnetism[35] since neither Hf^{4+} nor O^{2-} were magnetic ions, and the d and f shells of Hf^{4+} ions were either empty or full. In the past decade, many groups have been involved in this field in order to get a better understanding of d^0 magnetism. Actually, the RTFM has been observed in many kinds of undoped oxides, such as ZnO[36], SnO_2[37], TiO_2[38], and Al_2O_3[39], and is reported to be much sensitive to the growth conditions and considered to be strongly related to the defects within the materials. The influence on RTFM of various types of defects in DMO has been evaluated[40-42], such as structure defects, surface defects, strain, and point defects like vacancies and interstitials, but the divergent views leave it still an open question, and encourage us to conduct systematic research on a certain oxide. Zirconia (ZrO_2) is one of the most important ceramic materials with widespread application in structure materials, solid-state electrolytes, thermal barrier coatings, catalytic supports, oxygen gas sensors, and electro-optical materials[43-44]. It is known to have three low-pressure crystalline structures, i.e. monoclinic (m), tetragonal (t) and cubic (c). The monoclinic phase (space group $P2_1/c$), stable at RT, transforms to the tetragonal phase (space group $P4_2/nmc$) around 1 400 K, and then to cubic phase (space group $Fm3m$) around 2 570 K[45]. The c-ZrO_2 is predicted to be a promising candidate of DMO with Mn doping by theoretical calculation[46]. Since then, many groups have taken part in the investigation of ferromagnetism in doped and undoped ZrO_2, but obtain a series of contradicting conclusions. Table 1 presents a list of recent results of ZrO_2-based DMO[47-66], including the doping, crystalline structure, preparation method and magnetic order, which makes us much more interested in the magnetism in ZrO_2.

Table 1 Recent research work on the ZrO_2-based DMO

System	Phase	Preparation method	Magnetic order (RT)	Reference
Mn: ZrO_2	m/t/c	PLD	Ferromagnetic	[47-48]
Mn: ZrO_2	m/c	PLD	Ferromagnetic	[49]
Mn: ZrO_2	c	Chemical method	Ferromagnetic	[50]
Mn: ZrO_2	c	PLD	Ferromagnetic	[51]
Mn: ZrO_2	t	Sol-gel method	Ferromagnetic	[52]
Mn: ZrO_2	c	Coprecipitation	Nonmagnetic	[53]
Mn: ZrO_2	c	Chemical method	Nonmagnetic	[54]
Mn: ZrO_2	c	Sol-gel method	Nonmagnetic	[55]
Mn: ZrO_2	t	Solid state method	Nonmagnetic	[56]
Fe: ZrO_2	c	Microwave method	Ferromagnetic	[57]
Fe, Co: ZrO_2	t	Sol-gel method	Ferromagnetic	[58]
Fe: ZrO_2	t	Sol-gel method	Ferromagnetic	[59]
Fe: ZrO_2	c	Coprecipitation	Nonmagnetic	[53]
Fe: ZrO_2	m/t	Hydrothermal method	Nonmagnetic	[60]
Fe: ZrO_2	t/c	Freeze-drying method	Paramagnetic	[61]
Cu: ZrO_2	m/t	Incipient wetness impregnation	Paramagnetic	[62]
Ca: ZrO_2	c	Chemical citratecombustion	Ferromagnetic	[63]
Mg: ZrO_2	c	Chemical citratecombustion	Ferromagnetic	[63]
Undoped	m	PLD	Ferromagnetic	[47-48]
Undoped	m/t	Chemical citratecombustion	Ferromagnetic	[63]
Undoped	m	Purchased	Ferromagnetic	[64]
Undoped	m/t	PED	Ferromagnetic	[65]
Undoped	m/t	Sputtering	Ferromagnetic	[66]
Undoped	t	Sol-gel method	Ferromagnetic	[52]

In the following section, we will review our experimental work on the magnetism in ZrO_2 films without any dopants, which should be the first step to clarify whether ZrO_2 can exhibit ferromagnetism, and whether the ferromagnetism is intrinsic or not. In our work, based on the thorough analysis and characterization of intrinsic aspects, such as crystalline structure and oxygen defects, we are highly convinced that the intrinsic ferromagnetism in undoped ZrO_2 thin films is strongly dependent on the crystalline structure and can be enhanced by oxygen vacancy.

2 Experimental Section

To evaluate the effects of crystalline structure on the magnetism in ZrO_2 films, the high temperature phase of zirconia, i.e. *t*-ZrO_2 or *c*-ZrO_2, should be stabilized at RT firstly with non-doping methods, although doping is one of the most common ways to obtain the high temperature phase for traditional ZrO_2 ceramics[67-68]. Given that the *t*- or *c*-ZrO_2 may also be stabilized at RT by sufficient oxygen vacancy or confining the grain size to nanoscale in thin films or nanocrystals, different physical vapor deposition methods, such as pulsed electron beam deposition (PED), magnetron sputtering, and electron beam evaporation, have been utilized to prepare undoped ZrO_2 films. By adjusting the preparation parameters during the deposition process and post-annealing treatment, the manipulation of crystalline structure of ZrO_2 films has been achieved successfully.

PED is first used to prepare ZrO_2 films on <100> Si substrate[65]. It is observed that the ZrO_2 films with a thickness of ~100 nm exhibit a mixture of *m* and *t* phase, of which the ratio is dependent on the oxygen partial pressure during deposition (as shown in Fig.1). Specifically, for the ZrO_2 film deposited at an oxygen partial pressure of 9 mTorr, *m*-ZrO_2 is predominant, while for that deposited at higher oxygen partial pressure, the content of the *m*-ZrO_2 drastically decreases. We have also evaluated the influences on the ZrO_2 crystalline structure of others deposition parameters, such as substrate temperature and electron beam energy, but we still fail to obtain pure *m*- or *t*-ZrO_2 films, despite a significant manipulation of the two-phase ratio.

DC reactive magnetron sputtering is also utilized to prepare ZrO_2 films on <100> Si substrate[66]. The crystalline structure of the obtained ZrO_2 films strongly depends on the flow rate ratio between oxygen and argon during the sputtering process. In all cases, the thickness of ZrO_2 films was controlled at ~200 nm. From Fig.2, when deposited at an O_2/Ar ratio of 1/19, the crystalline structure seems to be close to hexagonal zirconium, indicating the oxygen partial pressure is not high enough to oxidize the metal Zr completely. The oxidation of zirconium is improved dramatically with the increase of the O_2/Ar ratio. When deposited at an O_2/Ar ratio of 2/18, the ZrO_2 films exhibit a nearly pure *t* phase, further confirmed by the good matching between the high-resolution transmission electron microscope (HRTEM) image and the schematic of the crystalline structure shown in Fig.3(a). When the ratio comes to 2.5/17.5, the *m*-ZrO_2 starts to appear, and then develops significantly with that increasing to 3/17. When that reaches 4/16, the ZrO_2 film seems to consist of only pure *m* phase, which can be also further confirmed by HRTEM image in Fig.3(b). The above results indicate the crystalline structure of ZrO_2 films may successfully be manipulated by adjusting the O_2/Ar ratio during preparation process, and that both of pure *m*- and *t*-ZrO_2 films can be stabilized at RT.

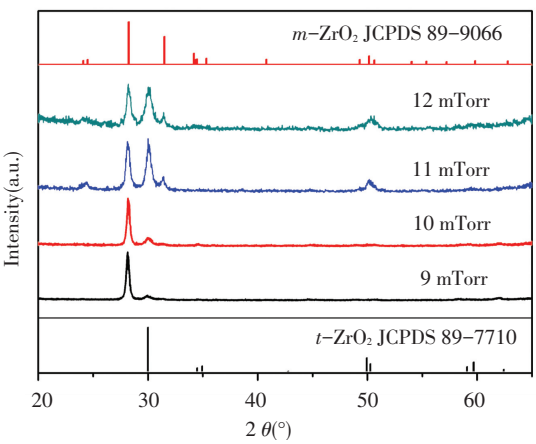


Fig.1 XRD results of ZrO_2 films prepared at different O_2 partial pressure by PED[65]

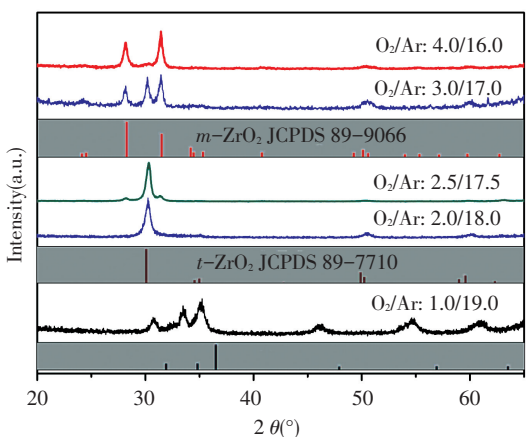
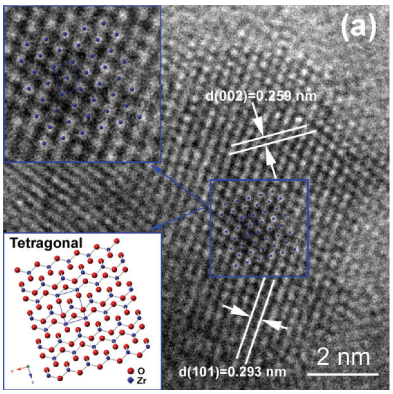
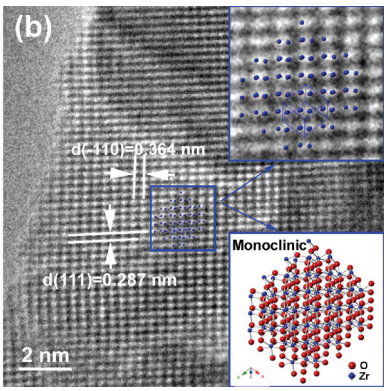


Fig.2 XRD results of ZrO_2 films prepared at different O_2/Ar ratio by sputtering[66]



(a) HRTEM images of tetragonal of ZrO_2 films



(b) HRTEM images of monoclinic of ZrO_2 films

Fig.3 HRTEM images of tetragonal and monoclinic of ZrO_2 films, in which the inset shows the schematic of the corresponding crystalline structure[69]

Electron beam evaporation is also used to prepare ZrO_2 films on < 100 > Si substrate. The as-grown 100 nm-thick films exhibit amorphous. In order to investigate the crystallization and phase transformation process of the amorphous ZrO_2 films, we conduct the in-situ optical reflectivity measurements based on the dependence of reflected optical power on the crystalline structure. Fig. 4 shows the in-situ reflected optical power versus the temperature, where the extreme point of the derivative of reflected power, specifically ~320 ℃ can be regarded as a crystallization or phase transformation point. Then, the as-grown films are annealed at 320 ℃ under air for 10 s, 10 min and 30 min respectively. XRD results demonstrate all the three annealed samples exhibit *t* phase, the high temperature one, unexpectedly. To assess the crystallization and phase transformation further, the as-grown films are annealed at 300 ℃, 500 ℃, 700 ℃, 900 ℃, and 1 050 ℃ for 10 s under air, respectively, by using rapid thermal annealing (RTA) system. The XRD results shown in Fig.5 indicate that the as-grown films still remain amorphous after annealing at 300 ℃, and crystallize fast and substantially into *t*-ZrO_2 after annealing at 320 ℃. With the increase of annealing temperature, a mixture of more *m*-ZrO_2 and less *t*-ZrO_2 is obtained. After annealed at 1 050 ℃, it exhibits nearly pure *m*-ZrO_2 ultimately. The above results not only pave a simple and effective way to manipulate the ZrO_2 film crystalline structure, but also reveal some interesting underlying physics of the crystallization and phase transformation of amorphous ZrO_2 films, which deserve much more attention in the future.

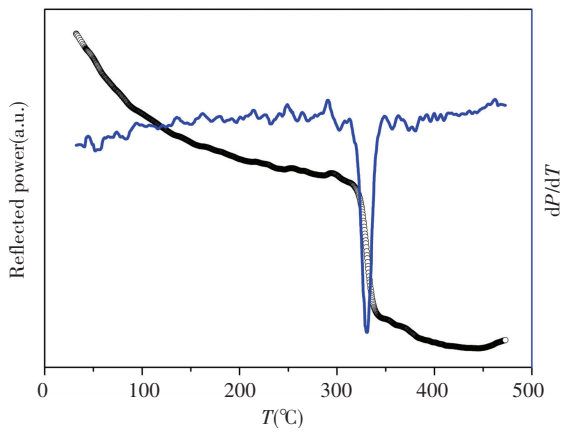


Fig. 4 The reflected optical power versus temperature of amorphous ZrO_2 films prepared by e-beam evaporation

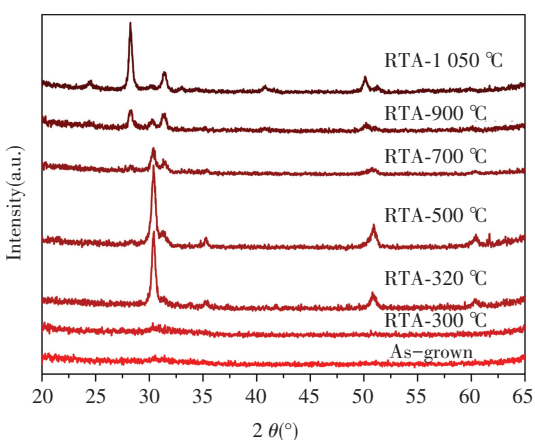


Fig. 5 XRD results of ZrO_2 films annealed at different temperature in air by RTA

3 Results and Discussions

3.1 Ferromagnetism in Undoped ZrO_2 Films

The RT in-plane magnetic properties of ZrO_2 films with different crystalline structure prepared with all the above three methods are characterized. Fig.6 shows the hysteresis loops of the ZrO_2 films deposited at different oxygen partial pressures by PED, indicating RTFM exists in all the samples, the ~100 Oe coercivity can be easily observed from the inset of Fig. 6, an enlargement of the hysteresis loop of sample deposited at 11 mTorr. Given the crystalline structure shown in Fig. 1, the normalized saturated magnetization (M_S)

seems to be positively dependent on the content of the *t* phase. Specifically, it is the minimum, ~ 0.04 emu/g, in the ZrO_2 film deposited at 9 mTorr in which *m* phase is predominant, and increases to the maximum, ~0.69 emu/g, in that deposited at 12 mTorr, in which the content of *t* phase is the largest.

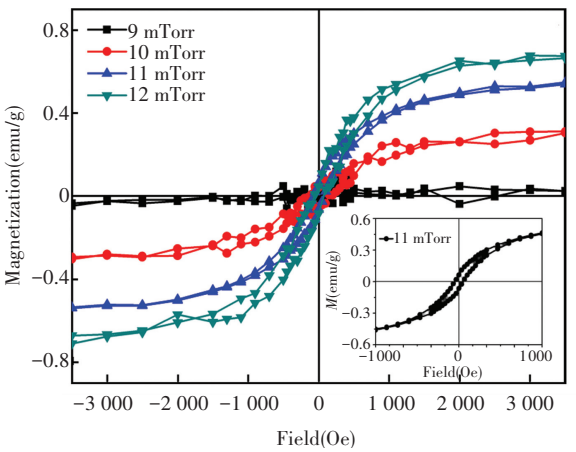


Fig.6 *M-H* curves of ZrO_2 films prepared at different O_2 partial pressure by PED[65]

As for the samples prepared by sputtering, three representative ones are selected for the RT magnetic measurements, i. e. ZrO_2 film with a crystalline structure of m phase, *t* phase and the mixture. All the above samples exhibit intrinsic RTFM with a coercivity of ~50 Oe shown in Fig.7. The M_S of *t*-ZrO_2 film is the largest, 0.19 emu/g, and then gradually weakens with the decrease of the content of *t* phase, and almost destroys when the film only consists of *m* phase. It demonstrates that the RTFM in undoped ZrO_2 films prepared by sputtering also strongly depends on the crystalline structure.

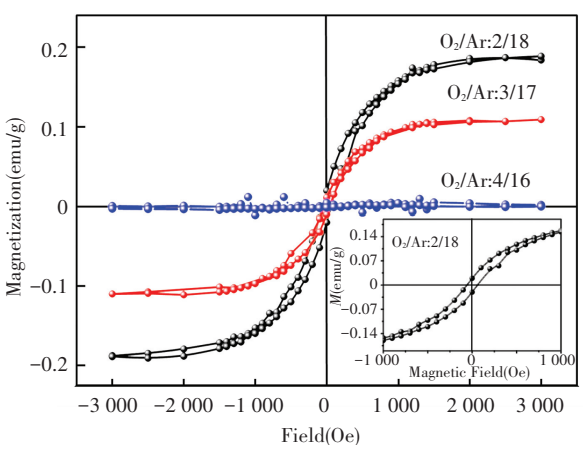


Fig.7 *M-H* curves of ZrO_2 films prepared at different O_2/Ar ratio by sputtering[66]

The RT magnetic properties of ZrO_2 films annealed at different temperature by RTA, which are prepared by e-beam evaporation originally, has been also characterized. From the results depicted in Fig. 8, a similar phase-dependent magnetism can be seen easily, that the normalized M_S is the largest for the ZrO_2 film with pure *t* phase, which is annealed at 320 ℃, and decreases gradually with decrease of *t* phase content, as a result of the increase of annealing temperature, and reaches the minimum for the sample with nearly pure *m* phase, which is annealed at 1 050 ℃.

Taking all the above magnetism results into consideration, we are much convinced that the RTFM can be present intrinsically within the undoped ZrO_2 films, and it is strongly dependent on the crystalline structure, specifically, *t* phase is much more active to the RTFM than the *m* one.

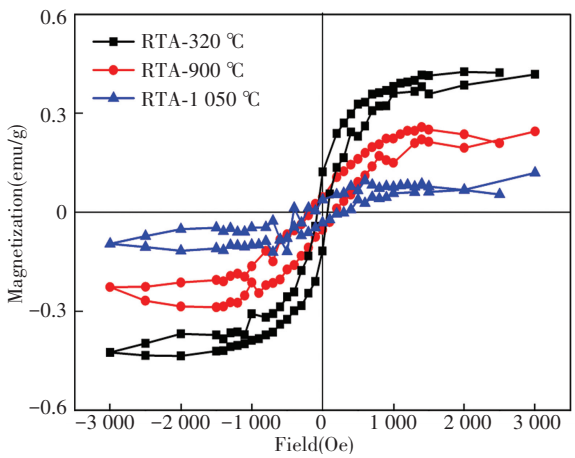


Fig.8 *M-H* curves of ZrO_2 films annealed at different temperature by RTA

3.2 Origin of Ferromagnetism in Undoped ZrO_2 Films

The non-equilibrium deposition process or the thermal annealing treatment can easily create various intrinsic defects that are predicted to be responsible for the unexpected d^0 magnetism in undoped DMO. A thorough defect analysis and characterization is of much necessity to evaluate the defect influence. Firstly, the high-resolution X-ray photoelectron spectroscopy (XPS) analysis on both of Zr 3*d* and O 1 *s* core level for the samples prepared by sputtering is conducted. The results shown in Fig.9 consistently suggest that all the three samples are oxygen-deficient and the increase of O_2/Ar ratio significantly enhances the oxidation. In other words, the number of oxygen vacancy drastically decreases from the maximum in the sample with a pure *t*-ZrO_2 film, to the minimum in that with a pure *m*-ZrO_2 as the O_2/Ar ratio increases from 2/18 to 4/16.

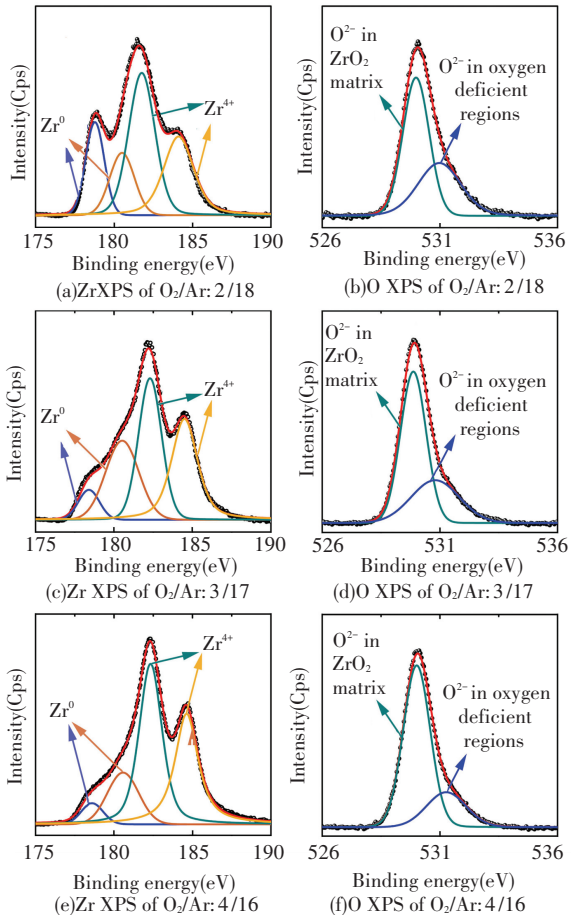
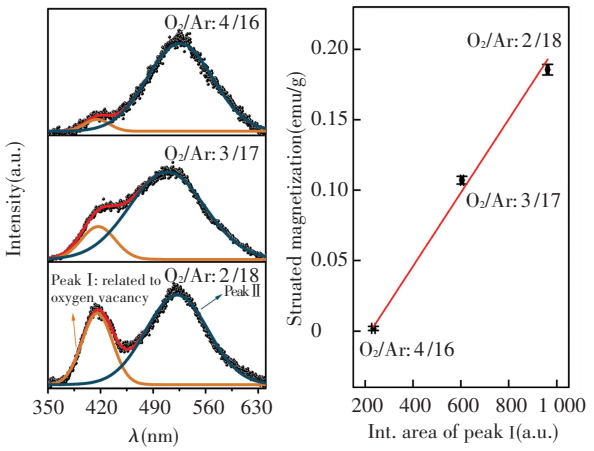


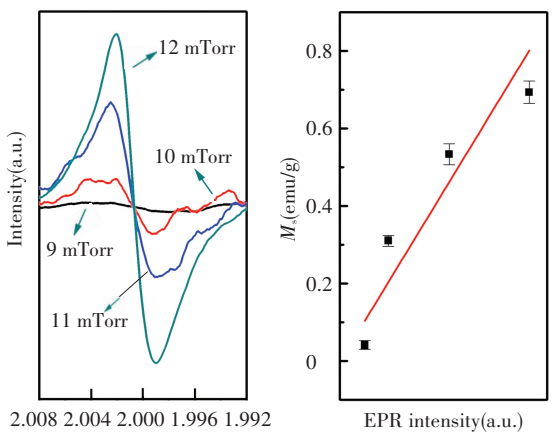
Fig.9 High resolution XPS of Zr 3d and O 1s core level of ZrO_2 films prepared at different O_2/Ar ratio by sputtering[66]

Photoluminescence (PL) experiments are then conducted on the same samples with XPS measurements, and it reveals that the emission ascribed to oxygen vacancy drastically weakens (see Fig.10(a)) in the ZrO_2 film deposited at a higher O_2/Ar ratio that consists of more *m* phase. The normalized M_S versus the intensity of PL emission originating from oxygen vacancy is plotted in Fig.10(b), where a good positive linear relationship can be easily observed, demonstrating the oxygen vacancy can significantly enhance the RTFM in undoped ZrO_2 films. The electron paramagnetic resonance (EPR) is also conducted on the samples prepared by PED to investigate the defect state in more detail. The result in Fig.11(a) shows that each sample exhibits a peak at a *g* factor of ~2.001 originating from singly ionized oxygen vacancy (V_O^+), a kind of typical paramagnetic defect[70], and that the intensity, corresponding to the number of V_O^+, is strongly dependent on the oxygen partial pressure. A positive correlation can be observed between the normalized M_S versus the EPR signal intensity (the height from peak to valley) from Fig.11(b), furthering confirming the ferromagnetism in undoped ZrO_2 films is strongly related to the oxygen vacancy, in particular the V_O^+.



(a) RT PL spectra of ZrO_2 films prepared at different O_2/Ar ratio by sputtering (b) The normalized M_S versus the integrated area of peak I in PL spectra ascribed to oxygen vacancy[66]

Fig.10 The relationship between magnetic property and PL results for the sputtering samples



(a) Normalized EPR spectra of ZrO_2 films prepared at different O_2 partial pressures by PED (b) the normalized M_S versus the EPR signal intensity[69]

Fig.11 The relationship between magnetic property and EPR results for the PED samples

Taking both structure and oxygen defect analysis into account, it seems that the RTFM in undoped ZrO_2 films is not only dependent on the crystalline structure, but also on the number of oxygen vacancy. In order to clarify their respective contribution to the ferromagnetism, further validation experiments are then conducted. Firstly, the sample consisting of only *t*-ZrO_2 prepared by sputtering is annealed at 350 ℃ in air for 1 h. After annealing, it still remains pure *t* phase, but the RTFM almost disappears (see Fig.12(b)). O 1*s*

core level XPS result after annealing shown in Fig.12 (a) suggests that oxygen deficiency is compensated to a large extent, indicating that the oxygen vacancy in t-ZrO_2 plays an important role in the origin or enhancement of RTFM in undoped ZrO_2 films. Likewise, the sample consisting of only m-ZrO_2 prepared by sputtering is also annealed at 350 ℃ in flowing Argon, an oxygen-deficient atmosphere, for 1 h. There are no changes in the crystalline structure, and no ferromagnetic signals appear in Fig.12(d), in spite of a significant reduction of ZrO_2 and increase of oxygen vacancy which can be seen from the O 1s core level XPS shown in Fig.12(c), indicating that the m-ZrO_2 could not exhibit ferromagnetic at RT even if it possesses a similar oxygen vacancy level with the t-ZrO_2. Then, it can be concluded that the intrinsic RTFM in undoped ZrO_2 films are indeed strongly dependent on the crystalline structure, and that t-ZrO_2 is much more active for the d^0 magnetism that is driven or enhanced significantly by the oxygen vacancy.

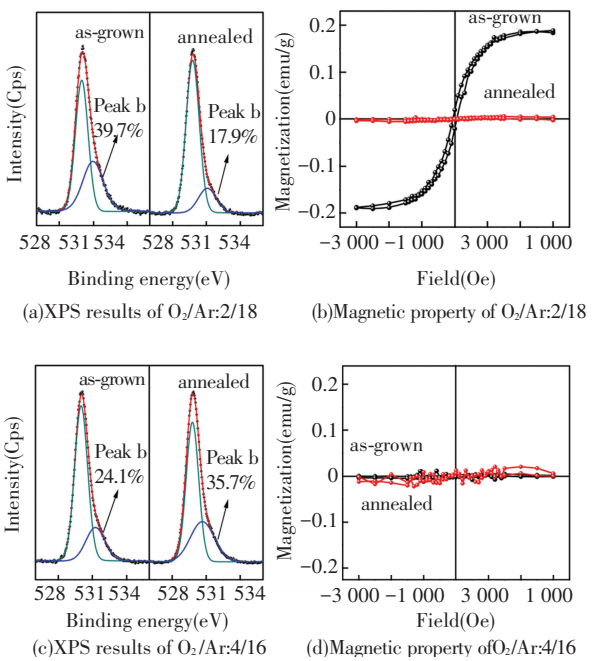


Fig.12 High resolution XPS of O 1s core level and M-H curves of the ZrO_2 films prepared at the O_2/Ar ratio of 2/18 and after annealed; high resolution XPS of O 1s core level and M-H curves of that prepared at the O_2/Ar ratio of 4/16 and after annealed[66]

Then, one may also have a better understanding of the slight difference of the M_S values among three different kinds of preparation methods, shown in Figs.6−8, which may result from several aspects. For instance, the thickness was different in the three cases, and defects, including oxygen vacancy, are much easier to be present in the region close to the interface. With the increase of film thickness, the crystallinity turns better and defects decrease drastically. That's why the samples prepared by sputtering with the larger thickness have lower M_S values. On the other hand, different preparation methods may result in a different number of oxygen vacancies within as-grown samples. As a consequence, the M_S may vary a little bit.

3.3 Mechanism of Oxygen Vacancy-Driven Ferromagnetism

Generally, two different theoretical models can be used to understand this oxygen vacancy-driven RTFM in DMOs, i.e. the percolation model of bound magneticpolaron (BMP)[34] and charge transfer ferromagnetism (CTF)[71]. For the BMP model, oxygen vacancy helps produce more BMPs and create a large overall volume occupied by BMPs. When the density of oxygen vacancy exceeds a certain threshold, it will lead to an overlap of BMPs and enhancing the ferromagnetic behavior[72]. However, this model could not give a reasonable explanation on the absence of ferromagnetism in monoclinic samples despite a large number of oxygen vacancies after annealing in flowing Ar. For the CTF model, the idea is that a narrow, structured local density of states $N_S(E)$ is associated with the defects, but the Fermi level will not normally locate as a peak in $N_S(E)$. A local charge reservoir, such as oxygen vacancies or cations with different charge states, provides a possibility for electron transfer to raise the Fermi level to a peak in the local density of states, leading to Stoner splitting of $N_S(E)$[73] and triggering the ferromagnetism. In other words, the CTF depends not only on the vacancy levels, but also on the electronic band structure and density of states. It may give us a new thinking about the phase-dependent RTFM that we observed in undoped ZrO_2 thin films. As reported, the electronic band structure of tetragonal ZrO_2 is significantly different from that of monoclinic one[74-76]. It is only in tetragonal ZrO_2 that the electron transferring from oxygen vacancies can raise the Fermi level to the peak in the local density of states and lead to spontaneous Stoner ferromagnetism, resulting in the different magnetic behavior between tetragonal and monoclinic samples with a similar oxygen vacancy level. Therefore, our results provide an experimental evidence for the CTF model to explain the magnetic ordering in undoped DMOs.

4 Conclusions

Undoped ZrO_2 film can be prepared by different physical vapor deposition, such as PED, sputtering

and e-beam evaporation. The crystalline structure can be manipulated successfully by adjusting the preparation parameters during the deposition process and post-annealing treatment. In particular, the high temperature phase, i.e. t-ZrO_2, can be stabilized at RT without any dopants, by sputtering at a proper oxygen partial pressure, or just annealing the amorphous samples prepared by e-beam evaporation at the critical crystallization temperature, which paves a simple way to investigate the phase-dependent properties of ZrO_2 films. Magnetic property characterization demonstrates that intrinsic ferromagnetism can be obtained in undoped ZrO_2 films, which seems to highly depend on the crystalline structure, as well as the oxygen defects in the films. Given the structure and defect analysis, the high temperature phase, i.e. t-ZrO_2, is found to be more active for the d^0 magnetism in undoped ZrO_2 films, and the ferromagnetism is strongly related with the oxygen vacancy.

In summary, in term of future applications, despite some progress of theoretical and experimental understanding, some details still remain unclear and appealing for much more attentions. Meanwhile, making use of DMO to design and fabricate prototype spintronic devices might also fascinate much more attention, which may become a new candidate for some new physical and multifunctional devices. We are pleased to see the progress of understanding of the d^0 magnetism and practical application of DMO in the near future.

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