ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理
Chinese Physics B

Homogeneous and inhomogeneous magnetic oxide semiconductors

Xiao-Li Li(李小丽), Xiao-Hong Xu(许小红)
Citation: Chin. Phys. B . 2019, 28(9): 098506 . **doi:** 10.1088/1674-1056/28/9/098506
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Two-dimensional XSe_2 (X=Mn, V) based magnetic tunneling junctions with high Curie temperature

Longfei Pan(潘龙飞), Hongyu Wen(文宏玉), Le Huang(黄乐), Long Chen(陈龙), Hui-Xiong Deng(邓惠雄), Jian-Bai Xia(夏建白), Zhongming Wei(魏钟鸣)
Chin. Phys. B . 2019, 28(10): 107504 . **doi:** 10.1088/1674-1056/28/10/107504

Magnetism induced by Mn atom doping in SnO monolayer

Ruilin Han(韩瑞林), Yu Yan(闫羽)
Chin. Phys. B . 2018, 27(11): 117505 . **doi:** 10.1088/1674-1056/27/11/117505

Oxide magnetic semiconductors：Materials, properties, and devices

Tian Yu-Feng, Hu Shu-Jun, Yan Shi-Shen, Mei Liang-Mo
Chin. Phys. B . 2013, 22(8): 088505 . **doi:** 10.1088/1674-1056/22/8/088505

The effect of dimerization on the magnetoresistance in organic spin valves

Wang Hui, Hu Gui-Chao, Ren Jun-Feng
Chin. Phys. B . 2013, 22(5): 058504 . **doi:** 10.1088/1674-1056/22/5/058504

The effects of electric and magnetic fields on the current spin polarization and magnetoresistance in a ferromagnetic/organic semiconductor/ferromagnetic (FM/OSC/FM) system

Wang Yu-Mei, Ren Jun-Feng, Yuan Xiao-Bo, Dou Zhao-Tao, Hu Gui-Chao
Chin. Phys. B . 2012, 21(10): 108508 . **doi:** 10.1088/1674-1056/21/10/108508

TOPICAL REVIEW — A celebration of the 100th birthday of Kun Huang

Homogeneous and inhomogeneous magnetic oxide semiconductors*

Xiao-Li Li(李小丽)[1,2] and Xiao-Hong Xu(许小红)[1,2,†]

[1] Key Laboratory of Magnetic Molecules & Magnetic Information Materials of Ministry of Education and School of Chemistry and Materials Science, Shanxi Normal University, Linfen 041004, China

[2] Research Institute of Materials Science of Shanxi Normal University and Collaborative Innovation Center for Shanxi Advanced Permanent Magnetic Materials and Technology, Linfen 041004, China

(Received 25 June 2019; revised manuscript received 24 July 2019; published online 23 August 2019)

Magnetic oxide semiconductors are significant spintronics materials. In this article, we review recent advances for homogeneous and inhomogeneous magnetic oxide semiconductors. In the homogeneous magnetic oxide semiconductors, we focus on the various doping techniques including choosing different transition metals, codoping, non-magnetic doping, and even un-doping to realize homogeneous substitution and the clear magnetic origin. And the enhancement of the ferromagnetism is achieved by nanodot arrays engineering, which is accompanied by the tunable optical properties. In the inhomogeneous magnetic oxide semiconductors, we review some heterostructures and their magnetic and transport properties, especially magnetoresistance, which are dramatically modulated by electric field in the constructed devices. And the related mechanisms are discussed in details. Finally, we provide an overview and possible potential applications of magnetic oxide semiconductors.

Keywords: magnetic oxide semiconductors, ferromagnetism, magnetoresistance

PACS: 85.75.–d, 75.50.Pp, 75.70.–i **DOI:** 10.1088/1674-1056/ab38ac

1. Introduction

Semiconductors and magnetic materials are two of the most important branches of condensed matter physics, which have major roles in the modern information technology.[1] Semiconductor devices generally take advantage of the charge of electrons, whereas magnetic materials are used for recording information involving electron spin.[2] The emerging field of spintronics aims at integrating ferromagnetism (FM) into semiconductors, using both the charges and spins in one material system.[3,4] It offers opportunities for a new generation of devices combining standard microelectronics with spin-dependent effects, which has the potential advantages of non-volatility, increased data processing speed, decreased electric power consumption, and increased integration densities compared with conventional semiconductor devices.[4] One of the most promising ways to integrate FM into semiconductors is doping the semiconducting material with a certain concentration of transition metals (TMs), yielding the commonly known magnetic semiconductors.[5]

Looking upon the history back to the 1960s, EuO and EuS with rock-salt structure are the two representatives, which were studied extensively. And then, researchers began to concern the magnetically doped II–VI semiconductors such as (Zn,Mn)Se and (Cd,Mn)Te in the late 1970s. Since the discovery of III–V ferromagnetic semiconductors such as (In,Mn)As and (Ga,Mn)As in 1990s, many interesting phenomena have been observed in this model system, such as tunneling anisotropic magnetoresistance (MR),[6,7] current driven domain-wall motion,[8,9] current switching magnetization by spin–orbit torques,[10,11] and so on. However, their Curie temperature (T_c) still well below room temperature (RT) limits the applications.[12,13] Later, a theoretical prediction of T_c of p-type Mn-doped ZnO diluted magnetic semiconductors (DMSs) in excess of RT by Dietl *et al.*[14] opens an era for experimental attempts to prepare magnetic oxide semiconductors and the correspondingly computational work to explain and predict the related mechanisms. Currently, two decades have been spent on investigating various magnetic oxide semiconductors. On the one hand, DMSs by doping a semiconductor with small concentrations of TM elements have attracted considerable attention.[15–17] Great effort has been devoted to realizing a fully homogeneous substitution of TM in oxides, increase T_c, and enhance FM, *etc*. On the other hand, many researchers have focused on inhomogeneous magnetic semiconductors with high TM concentrations. A major research effort has been devoted to investigating their magnetic and MR properties.

In this work, we review the recent advances in homogeneous and inhomogeneous magnetic oxide semiconductors. In the part of homogeneous magnetic oxide semiconductors, we emphasize on various doping techniques, especially the concept of "noncompensated n–p codoping" and the construction

*Project supported by the National Key Research and Development Program of China (Grant No. 2017YFB0405703), the National Natural Science Foundation of China (Grant Nos. 61434002, 51571136, and 11274214), and the Special Funds of Sanjin Scholars Program, China.

†Corresponding author. E-mail: xuxh@sxnu.edu.cn

© 2019 Chinese Physical Society and IOP Publishing Ltd

of nanodot arrays, which improve the efficiency of homogeneous substitution of TM in oxides and enhance FM, respectively. In the part of inhomogeneous magnetic oxide semiconductors, we focus on the properties simultaneously modulated by electric field and magnetic one, and the construction of multilayered nanowires (NWs) devices to realize the multifunctionality, ultra-small dimensions, and low energy consumption in magnetic oxide semiconductors. It should be pointed out that it is almost impossible to describe all the work performed around the world owing to the rapid pace of studies in this field.

2. Homogeneous magnetic oxide semiconductors

2.1. Doping

To realize RT FM, various wide band-gap oxide semiconductors such as ZnO, In_2O_3, TiO_2, *etc*. have been chosen as hosts, and almost all 3d TM elements have been chosen as the dopants. Among many hosts, ZnO is a typical example since the valence of Zn (2+) and the ionic radius can be readily adopted by many 3d TM ions. Coey *et al.*[18,19] observed RT FM in (110) oriented ZnO films made from targets containing 5 at.% of Sc, Ti, V, Fe, Co, or Ni, but not Cr, Mn, or Cu ions. After that, Co-doped ZnO films are well studied. However, due to the small solubility of TM in ZnO, the origin of FM might be attributed to some magnetic impurities. Later, magnetic semiconductors based on host semiconductors with high solubility of TM ions are highly desirable. Fortunately, the solubility of Fe ions in the In_2O_3 host lattice was found to be as high as 20%;[20] this makes it a good system to obtain homogeneous magnetic semiconductors and study the underlying physics in them.[21–23] Anyway, some impurity phases still appeared in it.[24,25] In fact, in addition to the doped elements and the doping concentrations, the structures and magnetism of magnetic semiconductor films strongly depend on the preparation conditions, such as the depositional method, substrate type, substrate temperature, deposition atmosphere, and post-annealing in different atmospheres at different temperatures, *etc*.[15,16,26,27] So far, some reviews[15,16,26] have commonly focused on a summary and comparison of magnetic semiconductors obtained by different groups and the different experimental conditions used. So in this review article, the influence of these preparation conditions on microstructures and FM of magnetic semiconductors will not be discussed in details. It is noteworthy pointing out that Liu *et al.* proposed a novel unconventional design that oxidizing originally ferromagnetic metals/alloys to form new species of magnetic semiconductors.[28] A high T_c above 600 K is realized in the $Co_{28.6}Fe_{12.4}Ta_{4.3}B_{8.7}O_{46}$ magnetic semiconductor by introducing oxygen into a ferromagnetic metallic glass.[28]

Anyway, up to now, the experimental results are quite contradictory, which seems to arise from either the low quality of the samples or the poor reproducibility of the growth conditions. Another suspicion is that the FM might be caused by a secondary phase such as doping elements or their oxides rather than the substitution of TM ions. So a fully homogeneous substitution of TM in oxides is always desirable. A codoping technique, especially the concept of "noncompensated n–p codoping" was introduced in ZnO and In_2O_3 DMSs to enhance the solubility of TMs in oxide semiconductor hosts and avoid the occurrence of second phases.[29–31] This concept was first proposed using first-principles calculations in the Si and Ge system.[32] This system was energetically favorable and kinetically accessible to an interstitial Mn to occupy a substitutional site neighboring an n-type dopant, thereby increasing the concentration of the substitutional Mn ions. The concept is also validated by direct measurements of band gap narrowing, and correspondingly the enhancement of the visible-light photoactivity of TiO_2.[33] Introducing the concept of "noncompensated n–p codoping" in DMSs embodies two crucial advantages: On the one hand, the electrostatic attraction within the n–p dopant pair enhances both the thermodynamic and kinetic solubility; on the other hand, as we know, many reports favored the contribution of carrier exchange interactions to FM, which refers to interactions between localized magnetic moments that are mediated by free carriers in the system.[34] So the noncompensated nature of n–p pairs consisting of different number of acceptors and donors can also modulate carrier density, and further influence the FM of oxide systems. In our study, ZnO films codoped with Mn and Al or Mn and Ga were fabricated, in which Mn was used as the p-type, Al and Ga were n-type dopants.[29,30] In the Ga, Mn-codoped ZnO film, not only fully homogeneous substitution is obtained, but also the saturation magnetization (M_s) value is dramatically enhanced comparing with Mn-doped ZnO film. The sample exhibits the metallic behavior. Moreover, its M_s and resistivity are almost equal at 5 K and 300 K. These results imply that the electrons are very mobile whether the temperature is low or high, which may mediate the local polarized spin of Mn ions.[30]

Besides the pursuing homogeneous substitution, almost all reports about DMSs referred to the origin of magnetic ordering, which is significant for not only understanding the nature of DMSs, but also its potential applications in the field of spintronics. Some publications favored carrier exchange interactions, which are characterized by strong coupling between localized *d* electrons of TM ions and the extended carriers of oxides.[22,29,35] Yamada *et al.* even transformed a low-carrier paramagnetic (PM) state of Co-doped TiO_2 to a high-carrier FM state by applying a gate voltage of a few volts, thereby revealed the considerable roles of electron carriers in high-

temperature FM.[36] With the further investigations, FM interaction can be unambiguously observed in some oxides without free carriers but in a dielectric state, which demonstrates that carriers are not necessary for FM. So bound magnetic polarons (BMPs) model was proposed by Coey *et al.*[18,19] In contrast to the structurally superior single crystal TM-doped TiO_2 films with negligible FM, FM is observed in structurally defective TM-doped TiO_2 films.[37] We have also found the direct experimental evidence that the local interactions of Fe^{3+} ions adjacent to oxygen vacancy centers in Fe-substituted In_2O_3 are directly responsible for the RT FM.[38] Some groups constructed DMS-based resistive switching (RS) devices to reversibly and reproducibly modulate FM of DMSs by electrically-controlled the change of the number of oxygen vacancies.[39–41] The RS devices will be discussed in details in Subsection 3.2. From the broad spread of experimental data, each model has its merits in certain aspects. It is difficult to draw general conclusions about the nature of magnetic interactions in DMSs.

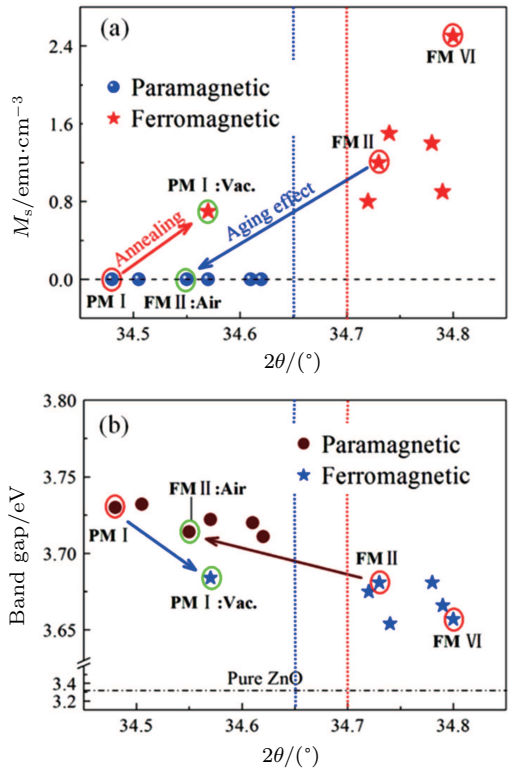


Fig. 1. The M_s (a) and band gap (b) measured at RT for the ZnMgO films as a function of the 2θ of ZnMgO (002) peak obtained from XRD data. The points for three representative films, PM I (in PM regime), FM II and FM VI (in FM regime) are labeled in red. Arrows lead from these points to their equivalent data points labeled in green. PM I: Vac represents PM I annealed in vacuum at 800 °C for 5 h; FM II: Air represents FM II placed in air for 6 months. Reprinted from Ref. [52]. Copyright (2017) with permission from Elsevier.

Up to now, more and more reports illuminate that defects are key factors for inducing FM in DMSs.[42–44] Some reports even observed the RT FM in non-magnetic-impurity-doped, and un-doped oxides, namely "d^0 ferromagnetism".[45–51] As this, the suspicion that FM is caused by a secondary phase can be avoided. We studied the relationship between RT FM and band gap tuning in ZnMgO films.[52] The films are crystallized in the hexagonal wurtzite phase and present a preferential (002) orientation with Mg^{2+} ions replacing Zn^{2+} ions of ZnO host matrix. Magnetism and the band gap are plotted against the position of (002) peak as shown in Fig. 1(a) and Fig. 1(b), respectively. It can be seen from Figs. 1(a)–1(b) that there may be relationship between RT FM, band gap, and microstructure in our ZnMgO films. Further analysis illustrates that both RT FM and band gap of the films are simultaneously tuned by the concentration of oxygen vacancies, which was further confirmed to be singly occupied oxygen vacancies (V_O^+). V_O^+ having the localized magnetic moments forms BMPs, which overlap each other resulting in a long-range FM ordering. Moreover, V_O^+ may lead to the formation of impurity band in the vicinity of valence band, which narrows the band gap.[52] Liu *et al.* designed electrically-controlled devices to modulate FM of SnO_2 films, which results from the formation/rupture of oxygen vacancy filaments, containing V_O^+ oxygen vacancies.[53]

2.2. Nanodot arrays

Lots of studies have mainly focused on the thin film, bulk, and polycrystalline powders of magnetic semiconductors. As advanced devices call for smaller nanostructured systems, the fabrication of lower-dimensional magnetic semiconductor structures is flourishing due to their unique advantages as well as smaller size, possible magnetic and optical properties. We fabricated ordered Fe-doped In_2O_3 and Fe–Sn codoped In_2O_3 nanodot arrays with different sizes using pulsed laser deposition (PLD) with the aid of ultrathin porous anodized aluminum oxide templates.[54,55] Figures 2(a)–2(h) show the morphology of Fe-doped In_2O_3 nanodot arrays with different average diameters of 80, 65, 50, and 35 nm.[54] All of them exhibit RT FM. Their M_s values increase as the dot sizes are reduced, rising to a maximum of about Fe ions of 15.30 μ_B/Fe [Fig. 3(a)] due to the surface effect. Moreover, the optical band width is also increased to 4.55 eV for the smallest dot

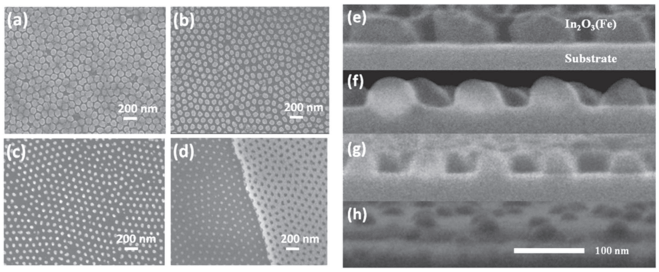


Fig. 2. SEM images for the Fe-doped In_2O_3 nanodot arrays. (a)–(d) The morphologies of nanodot arrays with average diameters of 80, 65, 50, and 35 nm and inter-dot distances of 105 nm. (e)–(h) The cross-sectional SEM images of corresponding nanodot arrays.[54] Copyright (2018) Springer Nature.

array as shown in Fig. 3(b), which may arise from the surface states due to Burstein–Moss effect.[54] For the Fe–Sn codoped In_2O_3 nanodot arrays, the obvious RT FM and the localized surface plasmon resonance band are observed. Moreover, they can be tuned by the Sn concentrations and sizes of nanodot arrays.[55] This combination of the magnetic and optical properties in a single material may be promising for future device applications.

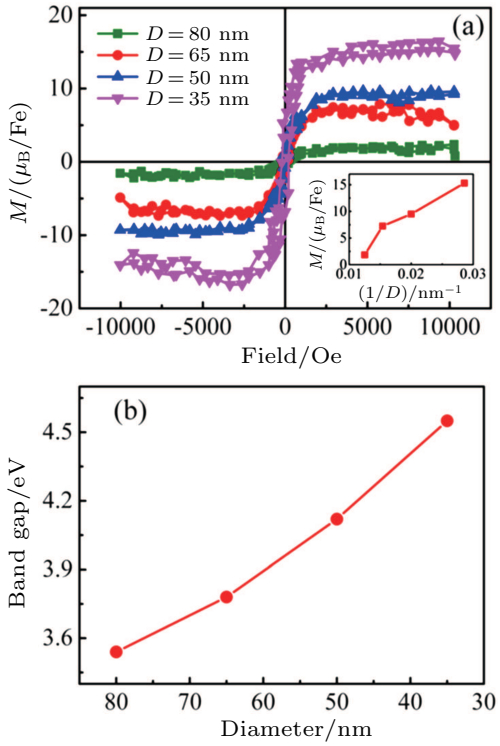


Fig. 3. (a) Hysteresis loops measured at 300 K for Fe-doped In_2O_3 nanodot arrays with different diameters (D). The inset shows the variation of M_s values with $1/D$; (b) The band gap of nanodot arrays as a function of D.[54] Copyright (2018) Springer Nature. The unit 1 Oe = 79.5775 A·m^{-1}.

3. Inhomogeneous magnetic oxide semiconductors

3.1. Magnetism and magnetoresistance

The promising FM and the clear origin of FM are always two key aims in studying magnetic semiconductors. From the above discussion, constructing nanodot arrays can dramatically enhance FM. Various methods including "noncompensated n–p codoping" and "d^0 ferromagnetism" are also proposed to avoid the controversy over whether the apparent FM arises from blocked particles of nanophases. As typical examples of ZnO-based magnetic semiconductors, Co-doped ZnO samples are extensively studied. The aim was always to grow films without ferromagnetic Co nanoparticles so as to be sure to observe true oxide magnetism. In contrast with the conventional work, we grew a Co, Al-doped ZnO film containing a significant fraction of Co nanoparticles, and observed FM. It is interesting that the nanoparticles contribute only a small fraction of the total magnetization, nevertheless, cause the whole sample to exhibit a large coercive field (H_c) at 5 K and remanence magnetization (M_r) through the exchange-coupling mechanism.[56] Hence, the startling results imply that incorporating controlled quantities of Co nanoparticles can improve the magnetic properties of the oxide.

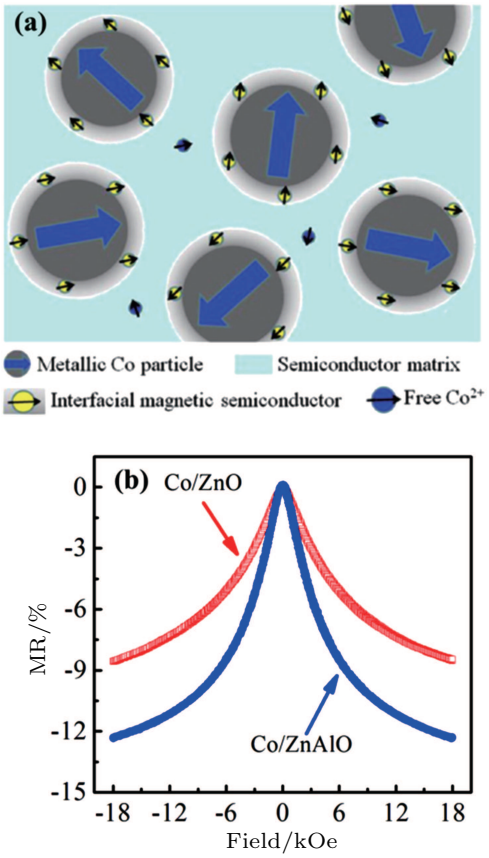


Fig. 4. (a) Schematic illustration of the granular films consisting of Co particles, semiconductor matrix, and the interfacial magnetic semiconductors. (b) MR measured at RT as a function of field for ZnO–Co and ZnAlO–Co films. Reprinted with permission from Ref. [66]. Copyright (2013) American Chemical Society.

In fact, besides magnetic properties, the potential applications of spintronics also motivate research about MR properties. Generally, MR in homogeneous magnetic semiconductors can always be observed at low temperatures.[29,30,57–59] Xu *et al.* even designed ZnCoO/Al_2O_3/Co magnetic tunnel junctions (MTJs), and observed a clear tunneling MR effect at 5 K, which demonstrates the spin injection from Co-doped ZnO to the crystallized Al_2O_3 and tunneling through the amorphous Al_2O_3.[60] Some inhomogeneous magnetic semiconductors, and even oxide-based granular films were also designed to investigate MR. Yan *et al.*[61,62] prepared ZnO–Co and TiO_2–Co inhomogeneous magnetic semiconductor films with high Co concentrations. They exhibited RT FM and large negative MR, which may be related to spin-dependent variable range hopping. We studied ZnO–Co and ZnAlO–Co films with Co concentrations from 20% to 60% by alternately sputtering Co layers and ZnO or ZnAlO layers.[63–66] The ZnO–Co

and ZnAlO–Co films consist of metallic Co particles, semiconductor matrix, and an interfacial magnetic semiconductor with the substitution of Co^{2+} for Zn^{2+} in the ZnO lattice at the interface between Co particles and the semiconductor matrix as shown in Fig. 4(a). Compared with −8.4% of the ZnO–Co film, the negative MR value of the ZnAlO–Co film reaches −12.3% at RT as shown in Fig. 4(b) and the corresponding spin polarization of tunneling electrons is about 37.5%. The enhanced spin injection from a metal into a semiconductor may be due to the formation of the magnetic semiconductors at the interface between the metallic Co particles and the semiconductor matrix in the granular films, which can act as a spin filter.[66] We also designed novel ZnO–Co samples with sandwich structures containing a layer of ZnO with Co nanoparticles that are blocked at RT separated by a ZnO spacer from a layer of ZnO containing superparamagnetic Co nanoparticles.[67] Magnetic interactions between the two ZnO–Co layers can be modulated by the pure ZnO spacer layer. A very large coupling is observed when the thickness of the ZnO spacer was reduced to zero so that the M_s of the sample was increased over the value expected from taking the sum of the two component films by a factor of over 10 at RT.[67] The above oxide-based nanostructures possess better compatibility with CMOS technology, which will provide an alternative opportunity for spintronics applications.

3.2. Electrically-controlled magnetism and magnetoresistance

A major research effort has been devoted to optimizing the magnetic and MR properties of homogeneous and inhomogeneous magnetic oxide semiconductors in the past two decades. At the same time, employing nonmagnetic means to switch and modulate magnetism becomes a requisite. Up to now, it is found that almost all magnetic materials have the potential to be controlled by electric fields.[68] FM of some oxide semiconductors can be induced by constructing electric double layer transistor geometry with charge carrier accumulation.[36] Nanoscale ion migration stimulated by external electric field provides alternative possibilities for introducing the desired modulation in materials' stoichiometries, defect profiles and magnetism and MR properties.[69] In particular, the ion-based RS devices with electrode/insulator (or semiconductor)/electrode sandwich structures can be freely programmed into a high resistance state (HRS) or a low resistance state (LRS) under external electrical stimuli for information storage applications.[70–73] Besides the RS behaviors, the devices can respond to magnetic, optical, and other stimuli for novel electronic device applications. FM of oxides as well as ZnO, TiO_2, and SnO_2 has been effectively tuned by designing RS devices through electrically-controlled the migration of oxygen ions and the corresponding change of the number of oxygen vacancies.[39–41,49,53]

Owing to the localized or filamentary nature of the active region in most of the RS devices, variability is one of the major challenges facing these devices for real applications. The key to minimize the variability is to facilitate and control the formation of the filaments. It is found that dispersing metal nanodots or nanoparticles in oxide matrices can enhance the local electric field, which will facilitate the filament formation, decrease the operating voltages and significantly reduce randomness of the filaments, leading to a better switching performance.[74–78] As discussed above, metallic Co particles exist in our ZnO–Co films with high MR ratios. So we proposed a novel Pt/ZnO/ZnO–Co/Au device, in which the matrix combines a nanostructured ZnO–Co layer and a ZnO layer. The device shows bipolar RS characteristics, and the RT MR effect can be observed in the sample at HRS and LRS as shown in Figs. 5(a)–5(c).[79]

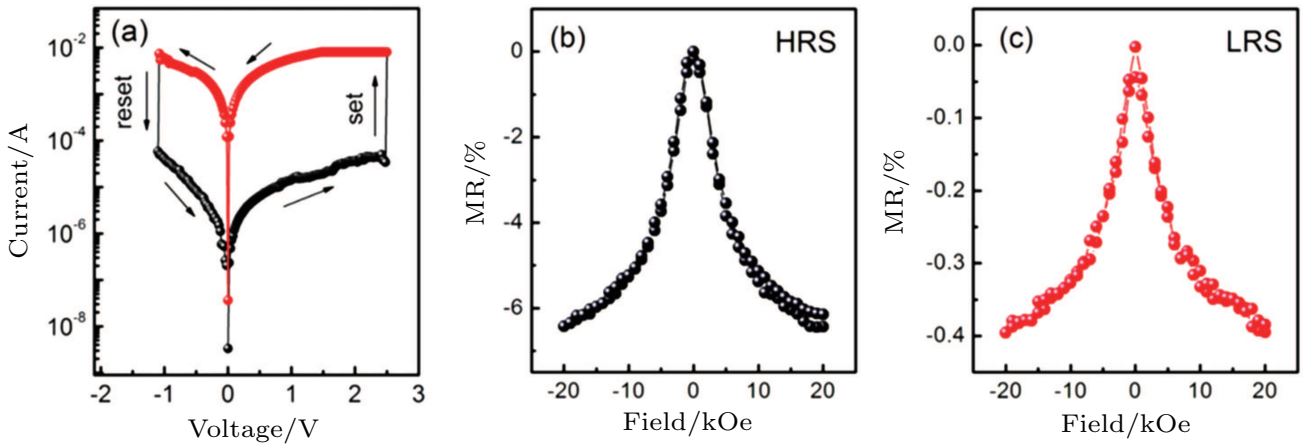


Fig. 5. (a) The *I*–*V* curve of the ZnO/ZnO–Co sample in a semi-logarithmic scale at RT. The arrows indicate the sweeping directions of the voltage. The field dependence of RT MR ratio of the sample at HRS (b) and LRS (c).[79] Copyright (2016) Springer Nature.

Through electric and magnetic control, four resistance states are realized in some oxide-based system such as ZnO and SiO_2.[79,80] The granular structure of the sample results in the large MR ratios at initial resistance state and HRS due to the spin-dependent tunneling between the regions of conducting magnetic Co through the ZnO or SiO_2 semiconducting barriers. When the sample was switched to LRS, it still exhibits a semiconductor behavior, which may demonstrate the migration of oxygen ions in ZnO and SiO_2 to top electrode under electric stimuli. The oxygen deficiency and the accumulation of oxygen vacancies in ZnO and SiO_2 resulting from the migration of oxygen ions during switching from HRS to LRS will weaken the insulating properties of the sample, reduce the possibility of the tunneling, and correspondingly result in the reduction of the MR.[79,80] Very recently, we even modulate MR and magnetic properties as well as M_s, H_c, and even M_r during RS process in an Au/ZnO–Co/SiO_2-Co/Pt structure, which may also be explained by the oxygen ion-migration effects coupled to redox reaction of Co nanoparticles in the film.[81] In fact, both MR and RS effects have also simultaneously realized in some oxide-based heterostructures. A reversible electric manipulation of RS and MR is observed in the Co/CoO–ZnO/Co MTJs due to the electric-field-driven migration of oxygen ions/vacancies between very thin CoO and ZnO layers.[82,83] In Co/ZnO/Fe sandwich structures, the formation of magnetic conductive filaments also constructed a nanoscale MTJ and induced tunneling MR in addition to the RS effect.[84]

Besides embedding some metal nanoparticles in the switching matrix, the one-dimensional (1D) oxide-based nanowires (NWs) are also a powerful approach to localize conducting paths within each nanowire and reduce the variability of the filaments.[85] Not only of this, the nanowires are crucial to reduce the size of the cells beyond the limitation of the current lithographic length scales in order to achieve high-density architecture and improve the performance of the devices.[86–88] However, most of the oxide nanowire-based devices usually require an electroforming process and high switching voltages,[85] which are not beneficial for reducing the power consumption. Inserting a metal layer into oxide nanowires and synthesizing partially oxidized nanowires are two typical ways to reduce the power consumption.[89–91] So we successfully designed multilayered NiO_x/Pt nanowire arrays, in which NiO_x implies partially oxidized. They are fabricated by a simple electrodeposition method combining a post-oxidization process.[92]

Figures 6(a)–6(b) show top and cross-sectional scanning electron microscope images of the pristine multilayered Ni/Pt nanowire arrays, respectively. Figure 6(c) compares X-ray diffraction patterns of the NW arrays before and after oxidization. Figures 6(d)–6(g) show the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of a NiO_x/Pt NW oxidized at 600 °C and the elemental maps of Ni, O, and Pt, respectively. Thus, partially oxidized NiO_x/Pt NW arrays with residual Ni nanoparticles are synthesized. They exhibit bipolar RS behavior with free-forming, low switching voltage. Moreover, MR, M_s, and H_c of the devices can be simultaneously tuned during the RS process as shown in Figs. 7(a)–7(d).[92] Realizing tunable magnetic and electrical properties in a simple device has received growing attention because of its multifunctionality and the possible broadening applications.

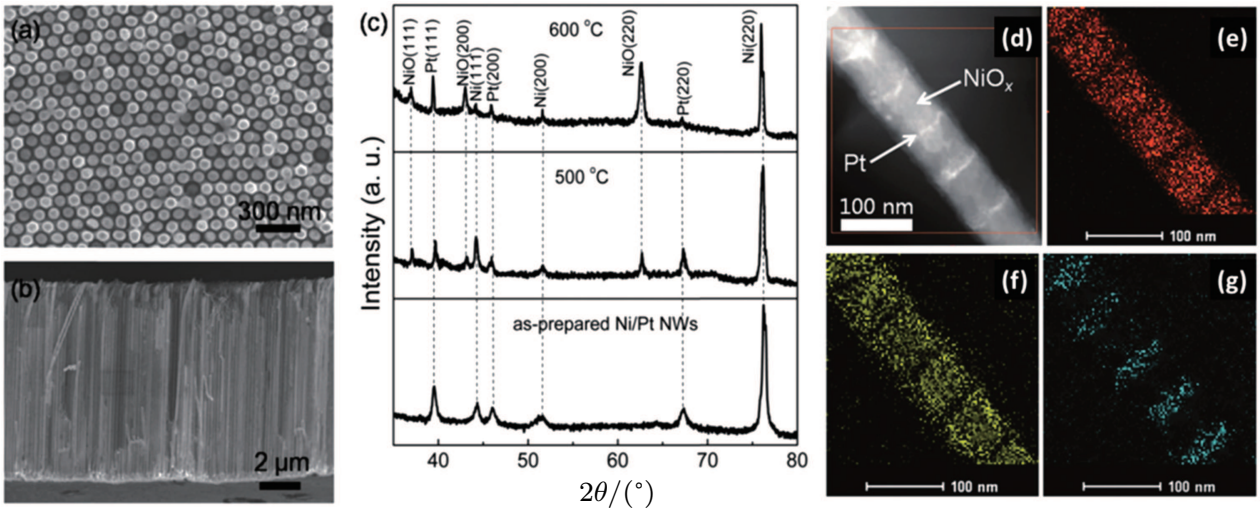


Fig. 6. (a) Top and (b) cross-sectional SEM images of the multilayered Ni/Pt NW arrays; (c) XRD patterns of the multilayered Ni/Pt NW arrays before and after oxidization; (d) HAADF–STEM image of NiO_x/Pt NWs oxidized at 600 °C and elemental maps of (e) Ni, (f) O, and (g) Pt.[92] Reproduced by permission of The Royal Society of Chemistry.

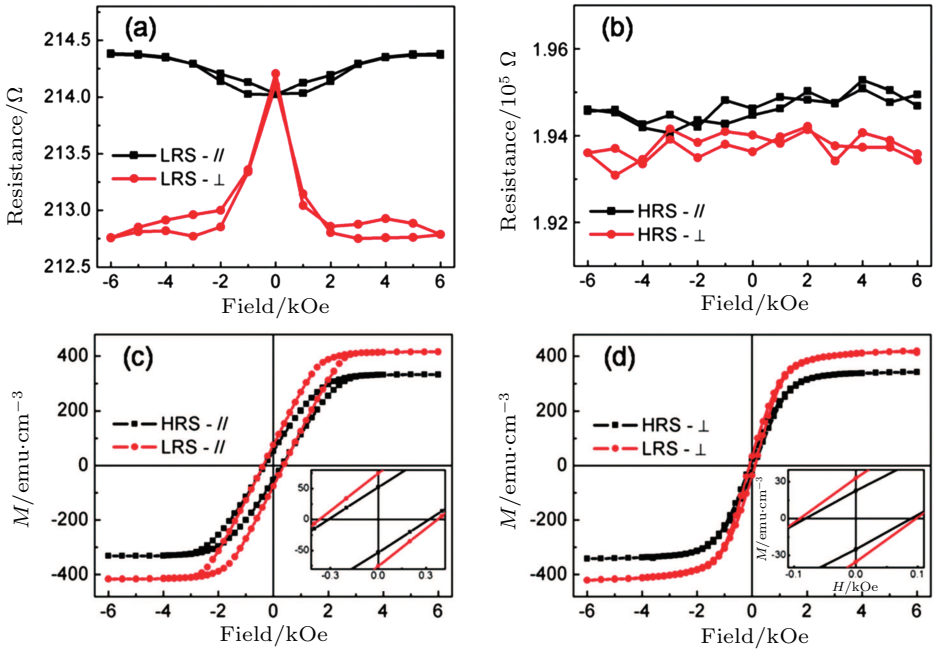


Fig. 7. MR of the NiO_x/Pt NW devices at the LRS (a) and HRS (b) with applied magnetic fields parallel and perpendicular to the NW axis; *M*–*H* curves of the NiO_x/Pt NW arrays at the HRS and LRS with applied magnetic fields parallel (c) and perpendicular (d) to the NW axis.[92] Reproduced by permission of The Royal Society of Chemistry.

4. Conclusion and perspectives

Dietl's prediction of T_c well above RT for oxide semiconductors has triggered intense interest in magnetic oxide semiconductors. Great efforts have been devoted to investigating various oxide semiconductors in order to realize RT FM. At first, the researchers focused on the homogeneous magnetic oxide semiconductors. Besides the preparation methods and conditions, various doping techniques including doping different TM elements, codoping, non-magnetic-impurity-doping, and even un-doping were used to obtain RT FM and the related mechanisms as well as carrier exchange interactions and BMPs model, *etc*. were investigated. Furthermore, nanodot arrays engineering can also enhance FM and even tune the optical properties. Different with conventional magnetic semiconductors with the homogeneous substitution, some magnetic nanoparticles may be dispersed in the inhomogeneous magnetic oxide semiconductors. They exhibit novel magnetic and MR properties. Moreover, these magnetic and MR properties can be dramatically modulated by designing some prototype spintronics devices, such as heterostructures, RS devices and constructing NWs.

In summary, homogeneous and inhomogeneous magnetic oxide semiconductors are significant multifunctional materials. Electrically-controlled their magnetic, transport, and even optical properties present new opportunities for spin-based device applications that may considerably affect future information-processing technologies. The results can pave the way for breakthroughs in basic research and the development of spintronics devices.

References

[1] Jungwirth T, Sinova J, Mašek J, Kučera J and MacDonald A H 2006 *Rev. Mod. Phys.* **78** 809
[2] Ohno H 1998 *Science* **281** 951
[3] Prinz G A 1998 *Science* **282** 1660
[4] Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnár S, Roukes M L, Chtchelkanova A Y and Treger D M 2001 *Science* **294** 1488
[5] Pearton S J, Abernathy C R, Overberg M E, Thaler G T, Norton D P, Theodoropoulou N, Hebard A F, Park Y D, Ren F, Kim J and Boatner L A 2003 *J. Appl. Phys.* **93** 1
[6] Gould C, Rüster C, Jungwirth T, Girgis E, Schott G M, Giraud R, Brunner K, Schmidt G and Molenkamp L W 2004 *Phys. Rev. Lett.* **93** 117203
[7] Wunderlich J, Jungwirth T, Kaestner B, Irvine A C, Shick A B, Stone N, Wang K Y, Rana U, Giddings A D, Foxon C T, Campion R P, Williams D A and Gallagher B L 2006 *Phys. Rev. Lett.* **97** 077201
[8] Yamanouchi M, Chiba D, Matsukura F and Ohno H 2004 *Nature* **428** 539
[9] Wang K Y, Edmonds K W, Irvine A C, Tatara G, Ranieri E D, Wunderlich J, Olejnik K, Rushforth A W, Campion R P, Williams D A, Foxon C T and Gallagher B L 2010 *Appl. Phys. Lett.* **97** 262102
[10] Chernyshov A, Overby M, Liu X Y, Furdyna J K, Lyanda-Geller Y and Rokhinson L P 2009 *Nat. Phys.* **5** 656
[11] Li Y Y, Cao Y F, Wei G N, Li Y Y, Ji Y, Wang K Y, Edmonds K W, Campion R P, Rushforth A W, Foxon C T and Gallagher B L 2013 *Appl. Phys. Lett.* **103** 022401
[12] Wang H L, Chen L and Zhao J H 2013 *Sci. Chin. Phys. Mech.* **56** 99
[13] Chen L, Yang X, Yang F H, Zhao J H, Misuraca J, Xiong P and von Molnár S 2011 *Nano Lett.* **11** 2584
[14] Dietl T, Ohno H, Matsukura F, Cibert J, Ferr and D 2000 *Science* **287** 1019
[15] Pan F, Song C, Liu X J, Yang Y C and Zeng F 2008 *Mater. Sci. Eng. R* **62** 1
[16] Li X L, Qi S F, Jiang F X, Quan Z Y and Xu X H 2013 *Sci. Chin. Phys. Mech.* **56** 111
[17] Tian Y F, Hu S J, Yan S S and Mei L M 2013 *Chin. Phys. B* **22** 088505
[18] Venkatesan M, Fitzgerald C B, Lunney J G and Coey J M D 2004 *Phys. Rev. Lett.* **93** 177206
[19] Coey J M D, Venkatesan M and Fitzgerald C B 2005 *Nat. Mater.* **4** 173
[20] Yoo Y K, Xue Q Z, Lee H C, Cheng S F, Xiang X D, Dionne G F, Xu S F, He J, Chu Y S, Preite S D, Lofl, S E and Takeuchi I 2005 *Appl. Phys. Lett.* **86** 042506

[21] Jiang F X, Xu X H, Zhang J, Wu H S and Gehring G A 2009 *Appl. Surf. Sci.* **255** 3655
[22] Xu X H, Jiang F X, Zhang J, Fan X C, Wu H S and Gehring G A 2009 *Appl. Phys. Lett.* **94** 212510
[23] Jiang F X, Xu X H, Zhang J, Fan X C, Wu H S, Alshammari M, Feng Q, Blythe H J, Score D S, Addison K, Al-Qahtani M and Gehring G A 2011 *J. Appl. Phys.* **109** 053907
[24] Jiang F X, Xi S B, Ma R R, Qin X F, Fan X C, Zhang M G, Zhou J Q and Xu X H 2013 *Chin. Phys. Lett.* **30** 047501
[25] Jiang F X, Feng Q, Quan Z Y, Ma R R, Heald S M, Gehring G A and Xu X H 2013 *Mater. Res. Bull.* **48** 3178
[26] Janisch R, Gopal P and Spaldin N A 2005 *J. Phys.: Condens. Matter* **17** R657
[27] Xia Y Q, Sun L, Xu H, Han J W, Zhang Y B, Wang Y and Zhang S D 2014 *Chin. Phys. Lett.* **31** 027501
[28] Liu W J, Zhang H X, Shi J A, Wang Z C, Song C, Wang X R, Lu S Y, Zhou X J, Gu L, Louzguine-Luzgin D V, Chen M W, Yao K F and Chen N 2016 *Nat. Commun.* **7** 13497
[29] Xu X H, Blythe H J, Ziese M, Behan A J, Neal J R, Mokhtari A, Ibrahim R M, Fox A M and Gehring G A 2006 *New J. Phys.* **8** 135
[30] Fan J P, Li X L, Quan Z Y and Xu X H 2013 *Appl. Phys. Lett.* **102** 102407
[31] Pan J, Wang S D, Zhang D Y, Hu J G, Chen Q and Wang J L 2013 *J. Appl. Phys.* **113** 043915
[32] Zhu W G, Zhang Z Y and Kaxiras E 2008 *Phys. Rev. Lett.* **100** 027205
[33] Zhu W G, Qiu X F, Iancu V, Chen X Q, Pan H, Wang W, Dimitrijevic N M, Rajh T, Meyer I I I H M, Paranthaman M P, Stocks G M, Weitering H H, Gu B H, Eres G and Zhang Z Y 2009 *Phys. Rev. Lett.* **103** 226401
[34] Zener C 1951 *Phys. Rev.* **81** 440
[35] Zeng Z T, Jiang F X, Ji L F, Zheng H Y, Zhou G W and Xu X H 2018 *RSC Adv.* **8** 31382
[36] Yamada Y, Ueno K, Fukumura T, Yuan H T, Shimotani H, Iwasa Y, Gu L, Tsukimoto S, Ikuhara Y and Kawasaki M 2011 *Science* **332** 1065
[37] Kaspar T C, Heald S M, Wang C M, Bryan J D, Droubay T, Shutthanandan V, Thevuthasan S, McCready D E, Kellock A J, Gamelin D R and Chambers S A 2005 *Phys. Rev. Lett.* **95** 217203
[38] Green R J, Regier T Z, Leedahl B, McLeod J A, Xu X H, Chang G S, Kurmaev E Z and Moewes A 2015 *Phys. Rev. Lett.* **115** 167401
[39] Chen G, Song C, Chen C, Gao S, Zeng F and Pan F 2012 *Adv. Mater.* **24** 3515
[40] Ren S X, Sun G W, Zhao J, Dong J Y, Wei Y, Ma Z C, Zhao X and Chen W 2014 *Appl. Phys. Lett.* **104** 232406
[41] Ren S Q, Qin H W, Bu J P, Zhu G C, Xie J H and Hu J F 2015 *Appl. Phys. Lett.* **107** 062404
[42] Ali N, Singh B, Khan Z A, Vijaya A R, Tarafder K and Ghosh S 2019 *Sci. Rep.* **9** 2461
[43] Bhakta N and Chakrabarti P K 2019 *J. Magn. Magn. Mater.* **485** 419
[44] Xia D Y, Hou Q Y and Guan Y Q 2019 *J Supercond. Nov. Magn.*
[45] Venkatesan M, Fitzgerald C B and Coey J M D 2004 *Nature* **430** 630
[46] Banerjee S, Mandal M, Gayathri N and Sardar M 2007 *Appl. Phys. Lett.* **91** 182501
[47] Li X L, Xu X H, Quan Z Y, Guo J F, Wu H S and Gehring G A 2009 *J. Appl. Phys.* **105** 103914
[48] Li X L, Guo J F, Quan Z Y, Xu X H and Gehring G A 2010 *IEEE T. Magn.* **46** 1382
[49] Bu J P, Liu X R, Hao Y M, Zhou G J, Cheng B, Huang W, Xie J H, Zhang H, Qin H W and Hu J F 2018 *Appl. Phys. Lett.* **112** 162408
[50] Agarwal D C, Singh U B, Gupta S, singhal R, Kulriya P K, Singh F, Tripathi A, Singh J, Joshi U S and Avasthi D K 2019 *Sci. Rep.* **9** 6675
[51] Lin Q L, Li G P, Xu N N, Liu H, E D J and Wang C L 2019 *J. Chem. Phys.* **150** 094704
[52] Quan Z Y, Liu X, Qi Y, Song Z L, Qi S F, Zhou G W and Xu X H 2017 *Appl. Surf. Sci.* **399** 751
[53] Liu X R, Bu J P, Ren X, Cheng B, Xie J H, Chen L B, Gao C Y, Liu L, Zhang H, Zhou G J, Qin H W and Hu J F 2019 *J. Magn. Magn. Mater.* **475** 368
[54] Jiang F X, Chen D, Zhou G W, Wang Y N and Xu X H 2018 *Sci. Rep.* **8** 2417
[55] Wang Y N, Jiang F X, Yan L J and Xu X H 2018 *Appl. Surf. Sci.* **441** 415
[56] Feng Q, Dizayee W, Li X L, Score D S, Neal J R, Behan A J, Mokhtari A, Alshammari M S, Al-Qahtani M S, Blythe H J, Chantrell R W, Heald S M, Xu X H, Fox A M and Gehring G A 2016 *New J. Phys.* **18** 113040
[57] Wang J, Gu Z B, Lu M H, Wu D, Yuan C S, Zhang S T, Chen Y F, Zhu S N and Zhu Y Y 2006 *Appl. Phys. Lett.* **88** 252110
[58] Xu Q Y, Hartmann L and Schmidt H 2007 *Phys. Rev. B* **76** 134417
[59] Wang D F, Ying Y, Thuy V T T, Kim J M, Seo M S, Gao F, Zhang T J, Kim K W and Lee Y P 2011 *Thin Solid Films* **520** 529
[60] Xu Q Y, Hartmann L, Zhou S Q, Mcklich A, Helm M, Biehne G, Hochmuth H, Lorenz M, Grundmann M and Schmidt H 2008 *Phys. Rev. Lett.* **101** 076601
[61] Yan S S, Ren C, Wang X, Xin Y, Zhou Z X, Mei L M, Ren M J, Chen Y X, Liu Y H and Garmestani H 2004 *Appl. Phys. Lett.* **84** 2376
[62] Yan S S, Liu J P, Mei L M, Tian Y F, Song H Q, Chen Y X and Liu G L 2006 *J. Phys.: Condens. Matter* **18** 10469
[63] Li X L, Quan Z Y, Xu X H, Wu H S and Gehring G A 2008 *IEEE T. Magn.* **44** 2684
[64] Quan Z Y, Xu X H, Li X L, Feng Q and Gehring G A 2010 *J. Appl. Phys.* **108** 103912
[65] Quan Z Y, Liu W, Li X L, Xu X H, Addison K, Score D S and Gehring G A 2011 *Mater. Lett.* **65** 2982
[66] Quan Z Y, Zhang X P, Liu W, Li X L, Addison K, Gehring G A and Xu X H 2013 *ACS Appl. Mater. Interfaces* **5** 3607
[67] Li X L, Jia J, Gao Y, Gehring G A and Xu X H 2015 *SPIN* **5** 1540008
[68] Song C, Cui B, Li F, Zhou X J and Pan F 2017 *Prog. Mater. Sci.* **87** 33
[69] Chen Q L, Liu G, Gao S, Yi X H, Xue W H, Tang M H, Zheng X J and Li R W 2019 *MRS Commun.* **9** 14
[70] Waser R, Dittmann R, Staikov G and Szot K 2009 *Adv. Mater.* **21** 2632
[71] Zhu X J, Shang J and Li R W 2012 *Front. Mater. Sci.* **6** 183
[72] Yang J J, Strukov D B and Stewart D R 2013 *Nat. Nanotechnol.* **8** 13
[73] Pan F, Gao S, Chen C, Song C and Zeng F 2014 *Mater. Sci. Eng. R* **83** 1
[74] Chang W Y, Cheng K J, Tsai J M, Chen H J, Chen F, Tsai M J and Wu T B 2009 *Appl. Phys. Lett.* **95** 042104
[75] Liu C Y, Huang J J and Lai C H 2013 *Thin Solid Films* **529** 107
[76] Yoon J H, Han J H, Jung J S, Jeon W, Kim G H, Song S J, Seok J Y, Yoon K J, Lee M H and Hwang C S 2013 *Adv. Mater.* **25** 1987
[77] Choi B J, Torrezan A C, Norris K J, Miao F, Strachan J P, Zhang M X, Ohlberg Douglas A A, Kobayashi N P, Yang J J and Williams R S 2013 *Nano Lett.* **13** 3213
[78] Li X L, Shi Y N, Li J, Bai Y H, Jia J, Li Y C and Xu X H 2017 *Mater. Res. Express* **4** 036407
[79] Li X L, Jia J, Li Y C, Bai Y H, Li J, Shi Y N, Wang L F and Xu X H 2016 *Sci. Rep.* **6** 31934
[80] Li X L, Li Y C, Shi Y N, Du F F, Bai Y H, Quan Z Y and Xu X H 2017 *Mater. Lett.* **194** 227
[81] Du F F, Li Y C, Li X L, Yang J, Bai Y H, Quan Z Y, Liu C L and Xu X H 2019 *J. Magn. Magn. Mater.* **489** 165445
[82] Li Q, Shen T T, Cao Y L, Zhang K, Yan S S, Tian Y F, Kang S S, Zhao M W, Dai Y Y, Chen Y X, Liu G L, Mei L M, Wang X L and Grűnberg P 2015 *Sci. Rep.* **4** 3835
[83] Zhang K, Cao Y L, Fang Y W, Li Q, Zhang J, Duan C G, Yan S S, Tian Y F, Huang R, Zheng R K, Kang S S, Chen Y X, Liu G L and Mei L M 2015 *Nanoscale* **7** 6334
[84] Yang Z H, Zhan Q F, Zhu X J, Liu Y W, Yang H L, Hu B L, Shang J, Pan L, Chen B and Li R W 2014 *Europhys. Lett.* **108** 58004
[85] Kim S I, Sa Y H, Kim J H, Chang Y W, Kim N, Kim H and Yoo K H 2014 *Appl. Phys. Lett.* **104** 023513
[86] Herderick E D, Reddy K M, Sample R N, Draskovic T I and Padture N P 2009 *Appl. Phys. Lett.* **95** 203505
[87] Kim S I, Lee J H, Chang Y W, Hwang S S and Yoo K H 2008 *Appl. Phys. Lett.* **93** 033503
[88] Oka K, Yanagida T, Nagashima K, Tanaka H and Kawai T 2009 *J. Am. Chem. Soc.* **131** 3434
[89] Huang Y C, Chen P Y, Chin T S, Liu R S, Huang C Y and Lai C H 2012 *Appl. Phys. Lett.* **101** 153106
[90] Huang Y C, Chen P Y, Huang K F, Chuang T C, Lin H H, Chin T S, Liu R S, Lan Y W, Chen C D and Lai C H 2014 *NPG Asia Mater.* **6** e85
[91] Liang K D, Huang C H, Lai C C, Huang J S, Tsai H W, Wang Y C, Shih Y C, Chang M T, Lo S C and Chueh Y L 2014 *ACS Appl. Mater. Interfaces* **6** 16537
[92] Wang L F, Li X L, Xue W H, Quan Z Y, Qin X F, Wang F and Xu X H 2018 *J. Mater. Chem. C* **6** 1996