REVIEWS

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The predicaments and expectations in development of magnetic semiconductors

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Abstract: Over the past half a century, considerable research activities have been directing towards the development of magnetic semiconductors that can work at room temperature. These efforts were aimed at seeking room temperature magnetic semiconductors with strong and controllable *s*, *p*–*d* exchange interaction. With this *s*, *p*–*d* exchange interaction, one can utilize the spin degree of freedom to design applicable spintronics devices with very attractive functions that are not available in conventional semiconductors. Here, we first review the progress in understanding of this particular material and the dilemma to prepare a room temperature magnetic semiconductor. Then we discuss recent experimental progresses to pursue strong *s*, *p*–*d* interaction to realize room temperature magnetic semiconductors, which are achieved by introducing a very high concentration of magnetic atoms by means of low-temperature nonequilibrium growth.

Key words: magnetic semiconductors; *s*, *p*–*d* interaction; high concentration of magnetic atoms; low temperature nonequilibrium growth; semiconductor spintronics

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1. Introduction

Magnetic semiconductors[1, 2] have been pursued for more than 50 years because they combine two mainstream components of modern information technology, semiconductor for logic and magnetism for memory, within a single material. Owing to the capability of processing and retaining the logic states at the same time, a new type of computer made by magnetic semiconductors could possess nonvolatility of data, high speed of processing and low energy consumption, potentially changing the way we use digital devices[3, 4]. Extensive experimental and theoretical works were thus devoted to this subject. According to the Web of Science, more than 21 thousands articles can be found out up to 2019 if the term "Magnetic semiconductors" was selected as research topic. As shown in Fig. 1, a research boom can be observed at 2009, where the number of articles was boosted almost 5 times more than ten years before. There is no doubt that the study on magnetic semiconductors has evolved into an important field of physics and materials science.

Despite considerable research efforts, a magnetic semiconductor that exhibits usefully large, gateable spin polarizations at room temperature is still missing[5, 6]. The discovery of room temperature ferromagnetic semiconductors was proving to be a great challenge, which was regarded as one of the 125 critical unanswered scientific questions posed in *Science*: "Is it possible to create magnetic semiconductors that work at room temperature?"[7] It is very difficult because a useful magnetic semiconductors should have both characters simultaneously: strong *s*, *p*–*d* exchange interactions that persists to room temperature, as well as robust room temperature remnant magnetization. A strong coupling between free carriers (*s* or *p* electrons) and local spins (*d* electrons) is the essential character of magnetic semiconductors, which leads to spin-polarized carriers that give spintronics devices novel functionalities. Besides, in order to become a practical technology, remnant magnetization should be robust to allow spin-polarized currents to propagate in the materials without the need for a continuous magnetic field[8].

Unfortunately, neither of them has been demonstrated as a room temperature intrinsic magnetic semiconductor so far. Due to small feasibilities of application, the development of magnetic semiconductors slowed down. In recent years, publications on this subject declined rapidly, as shown in Fig. 1. When a scientific gold-rush excitement passed, it is a good time to think calmly about the ways for seeking room temperature magnetic semiconductors. Here, we would like to quote from Churchill: "This is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning." Indeed, this is not the first time that the study on magnetic semiconductors sank into a low valley. The question is still open, and a lot of rooms remain for people to exploit. In this review, we will start with a simple historical review to draw inspirations from the past. Then we discuss recent experimental progresses to pursue strong *s*, *p*–*d* interaction to realize room temperature magnetic semiconductors, which are achieved by introducing a very high concentration of magnetic atoms by means of low-temperature nonequilibrium growth.

2. A brief historical perspective on magnetic semiconductors

In history, the list of candidate magnetic semiconductors

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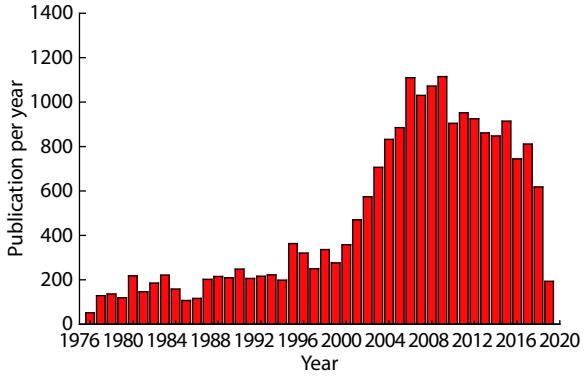

Fig. 1. (Color online) Publications per year on magnetic semiconductors according to the Web of Science. The term "Magnetic semiconductors" was selected as research topic.

Table 1. Composition range and crystal structure of II–VI magnetic semiconductors.

Alloy	Composition range	Crystal structure
$Zn_{1-x}Mn_xS$	$0.00 < x \leqslant 0.15$	Zinc blende
	$0.1 < x \leqslant 0.45$	Wurtzite
$Zn_{1-x}Mn_xSe$	$0.00 < x \leqslant 0.30$	Zinc blende
	$0.30 < x \leqslant 0.57$	Wurtzite
$Zn_{1-x}Mn_xTe$	$0.00 < x \leqslant 0.86$	Zinc blende
$Cd_{1-x}Mn_xS$	$0.00 < x \leqslant 0.50$	Wurtzite
	$0.94 < x \leqslant 1.00$	NaCl type
$Cd_{1-x}Mn_xSe$	$0.00 < x \leqslant 0.50$	Wurtzite
	$0.94 < x \leqslant 1.00$	NaCl type
$Cd_{1-x}Mn_xTe$	$0.00 < x \leqslant 0.77$	Zinc blende
	$0.96 < x \leqslant 1.00$	NiAs type
$Hg_{1-x}Mn_xS$	$0.00 < x \leqslant 0.37$	Zinc blende
$Hg_{1-x}Mn_xSe$	$0.00 < x \leqslant 0.38$	Zinc blende
$Hg_{1-x}Mn_xTe$	$0.00 < x \leqslant 0.75$	Zinc blende
$Zn_{1-x}Fe_xS$	$0.00 < x \leqslant 0.15$	Zinc blende
$Zn_{1-x}Fe_xSe$	$0.00 < x \leqslant 0.30$	Zinc blende
$Zn_{1-x}Fe_xTe$	$0.00 < x \leqslant 0.15$	Zinc blende
$Cd_{1-x}Fe_xSe$	$0.00 < x \leqslant 0.30$	Wurtzite
$Cd_{1-x}Fe_xTe$	$0.00 < x \leqslant 0.15$	Zinc blende
$Hg_{1-x}Fe_xSe$	$0.00 < x \leqslant 0.15$	Zinc blende
$Hg_{1-x}Fe_xTe$	$0.00 < x \leqslant 0.12$	Zinc blende
$Zn_{1-x}Co_xS$	$0.00 < x \leqslant 0.14$	Zinc blende
$Zn_{1-x}Co_xSe$	$0.00 < x \leqslant 0.05$	Zinc blende
$Cd_{1-x}Co_xSe$	$0.00 < x \leqslant 0.22$	Wurtzite

can be grouped into two categories: undoped magnetic semiconductors, such as europium chalcogenides and semiconducting spinels[9] that have a periodic array of magnetic elements on their own; and doped magnetic semiconductors, such as (Cd,Mn)Se[10] and (Ga,Mn)As[11], which are achieved by doping magnetic elements into conventional nonmagnetic semiconductors to make them ferromagnetic.

Undoped ferromagnetic semiconductors were extensively studied in the late 1960s to early 1970s. EuO, for example, is considered the first magnetic semiconductor, however, with a low Curie temperature (T_c) of only 77 K[12]. Besides the low T_c, crystal growth of these compounds is extremely difficult. To obtain even a small single crystal requires weeks of preparation and growth[11]. What is worse, the crystal structure of such magnetic semiconductors is quite different from that of Si and GaAs, so they cannot be incorporated into complex integrated circuits. On the other hand, doped magnetic semiconductors seemed to be more promising with regard to compatibility with modern semiconductor industry as well as tunability of the resulting magnetic properties.

2.1. II–VI magnetic semiconductors

II–VI compounds (such as CdTe, ZnTe, and CdSe) doped with transition metal (TM) elements (such as Mn) have been studied quite extensively in the 1980s[10, 13, 14]. The possible composition range and crystal structure of II–VI ferromagnetic semiconductors are shown in Table 1[15]. Although magnetic ions can be introduced into II–VI semiconductors up to 40%–50%, the II–VI ferromagnetic semiconductors are predominantly antiferromagnetic or paramagnetic[10]. The overwhelming contribution to magnetism is the super-exchange mechanism, which can be viewed as an indirect exchange interaction mediated by the anion. In the presence of an external magnetic field, the Mn^{2+} ions become magnetized, and consequently the electrons and holes are effected by a large magnetization from the Mn^{2+} ions. This results in a Zeeman splitting that can be hundreds of times larger than that in non-magnetic semiconductor quantum structures. This, in turn, results in a giant Faraday rotation. The II–VI compounds therefore can be used as optical isolator[16]. However, the interest in II–VI magnetic semiconductors ebbed very quickly because of the lack of ferromagnetism, which was the first depression on this field.

2.2. III–V dilute magnetic semiconductors

III–V alloys, such as $Ga_{0.95}Mn_{0.05}As$, took centre stage in 1996[17], when Hideo Ohno's group demonstrated ferromagnetic order in this compound with T_c below 60 K, which, with improvements in the control of the material quality, has subsequently risen to 190 K[18]. This discovery struck an immediate chord with researchers interested in spintronic applications, as the host semiconductor GaAs is a mainstream semiconductor used in lasers, high-mobility transistors and other devices. By introducing Mn into this material it could lead to seamless electrical manipulation of magnetic states and magnetic modification of electrical or optical signals. For example, Hideo Ohno's group has already shown electrical control of ferromagnetism[19] (Fig. 2) and spin polarized electroluminescence[20] (Fig. 3) based (Ga,Mn)As. Furthermore, (Ga,Mn)As is able to provide interesting insights into a variety of spintronic phenomena, such as domain wall motion[21, 22], spin torque[23], spin Seebeck effect[24, 25], planar Hall effect[26], and tunnelling anisotropic magnetoresistance[27]. It is well accepted in the III–V dilute magnetic semiconductors that the long range ferromagnetic order between localized moments provided by substitutional Mn is mediated by the itinerate holes generated also by substitutional Mn through RKKY exchange coupling. Unfortunately, though the Curie temperature of Mn-doped GaAs has been greatly improved compared to previous II–VI group compounds, it is still far below room temperature[28, 29]. Substitution of divalent Mn atoms into trivalent Ga sites leads to severely limited chemical solubility (usually $\leqslant$ 5%). The heterovalent substitution, which simultaneously dopes both hole carriers and magnetic atoms, makes it difficult to individually control the local spin and carrier densities to enhance the effective p–d coupling that is necessary for a higher T_c.

2.3. Oxide magnetic semiconductors

In April 2000, Tomasz Dietl *et al.* published a theoretical paper in *Science* that provided a model to explain the origin of

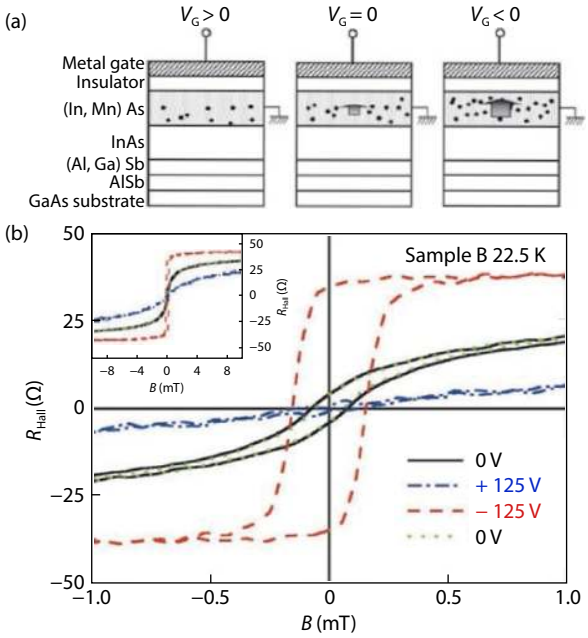

Fig. 2. (Color online) (a) Electric field control of the hole-induced ferromagnetism in magnetic semiconductor (In,Mn)As field-effect transistors. (b) Hall resistance versus field curves under three different gate biases. Inset, the same curves shown at higher magnetic fields. Reprinted with permission from Ref. [19]. Copyright (2000) by Springer Nature.

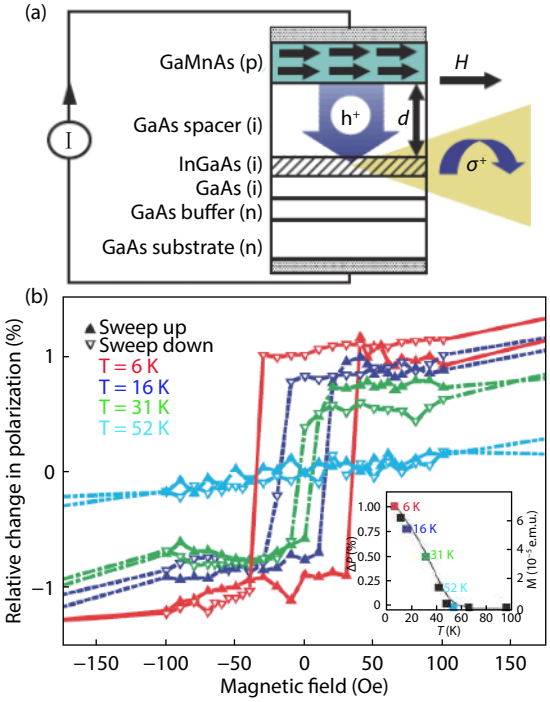

Fig. 3. (Color online) Electrical spin injection in an epitaxially grown ferromagnetic semiconductor heterostructure based on GaAs. (a) Spontaneous magnitization develops below the Curie temperature T_C in the ferromagnetic p-type semiconductor (Ga,Mn)As, depicted by the black arrows in the green layer. Under forward bias, spin-polarized holes from (Ga,Mn)As and unpolarized electrons from the n-type GaAs substrate are injected into the (In,Ga)As quantum well (QW, hatched region), through a spacer layer with thickness d, producing polarized electroluminescence. (b) Hysteretic electroluminescence polarization is a direct result of spin injection from the ferromagnetic (Ga,Mn)As layer. Inset, the relative remanent polarization shown in solid squares at T = 6–94 K. Reprinted with permission from Ref. [20]. Copyright (1999) by Springer Nature.

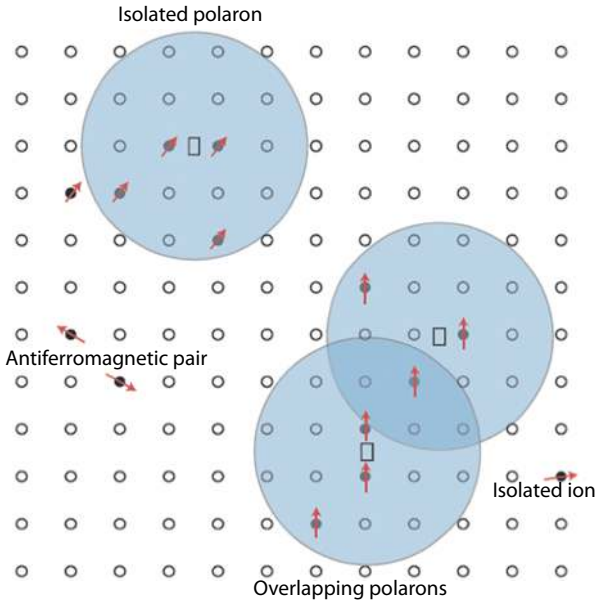

Fig. 4. (Color online) Representation of magnetic polarons. A donor electron in its hydrogenic orbit couples with its spin antiparallel to impurities with a 3d shell that is half-full or more than half-full. Cation sites are represented by small circles. Oxygen is not shown; the unoccupied oxygen sites are represented by squares. Small black balls with arrows represent magnetic ions. Reprinted with permission from Ref. [56]. Copyright (2005) by Springer Nature.

ferromagnetism in (Ga,Mn)As, and used the same model to predict ferromagnetism in wide bandgap materials ZnO and GaN[30]. They predicted that the ferromagnetism of ZnO-based magnetic semiconductors can persist above room temperature[30]. This marked the starting point of an exciting race for room temperature ferromagnetic semiconductors and pushed ZnO into the focus of materials research. Indeed, room temperature ferromagnetism has commonly been obtained in ZnO systems doped with transition metal elements such as V[31–33], Cr[34–36], Mn[37–42], Fe[43], Co[44–46], Ni[47, 48], and Cu[49, 50], and co-doping such as CoFe[51–53] and MnCo[54, 55]. Similar to (Ga,Mn)As, oxide magnetic semiconductor research was also confined to dilute magnetic compounds containing minute amounts of magnetic ions, owing to the very low thermodynamic miscibility (typically ⩽ 10%) of transition metals. These are the so-called dilute magnetic oxides. In order to explain why dilute magnetic oxides without itinerary carriers become ferromagnetic at room temperature, the concept of bound magnetic polarons was introduced[56]. In the bound magnetic polaron model, oxygen vacancies act as both electron donors and electron traps, which can bind the electrons and maintain insulating behavior. As shown in Fig. 4, each trapped electron couples the local moments of doped magnetic ions that lie within its orbit ferromagnetically, leading to a bound polaron with a large net magnetic moment. If neighboring polarons do not interact strongly, a paramagnetic, insulating phase will be resulted in. However, for certain polaron–polaron distances and combinations of electron–electron and electron–local-moment exchange constants, the polarons couple ferromagnetically.

Although a considerable amount of experimental data and corresponding mechanisms have been accumulated, the origin and control of ferromagnetism in dilute magnetic oxides are the most controversial research topic in materials sci-

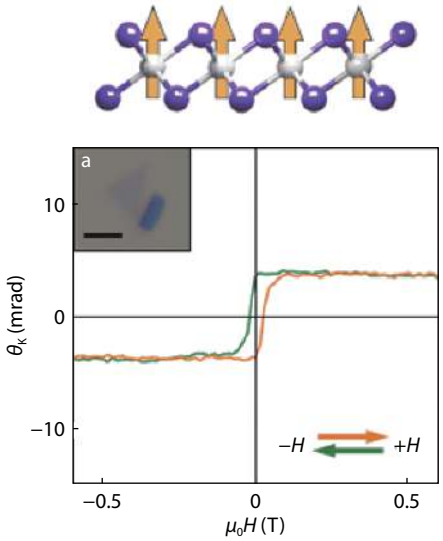

Fig. 5. (Color online) (a) Out-of-plane view of the CrI_3 structure depicting the Ising spin orientation. (b) Polar MOKE signal for a CrI_3 monolayer at a temperature of 15 K. The inset shows an optical image of an isolated monolayer (the scale bar is 2 μm). Reprinted with permission from Ref. [87]. Copyright (2017) by Springer Nature.

ence and condensed-matter physics. The data are notoriously plagued by instability and a lack of reproducibility[57, 58]. The weak magnetization displayed by thin-film specimens at room temperature is typically only 10 emu/cm^3. In particular, spin-polarized electrical transport is barely noticeable in such materials, because the coupling between the mobile carriers and the localized 3*d* electrons is very weak[59–61]. Many scientists are now convinced that Dietl's predictions on room temperature ferromagnetism are not realizable, due to unrealistic assumption of $Mn_{0.05}Zn_{0.95}O$ with hole concentration up to 3.5×10^{20} cm^{-3}[62, 63].

2.4. Two dimentional magnetic semiconductors

Since graphene was successfully prepared from graphite in 2004, two dimentional (2D) layered materials have received extensive attentions, which provided new opportunities to make 2D magnetic semiconductors. The first attempt was to add ferromagnetism to the long list of graphene's capabilities. One can imagine that the ferromagnetic graphene could lead to novel transport phenomena such as the quantized anomalous Hall effect[64], which is very promising for dissipationless transport[65]. From a theoretical point of view, magnetic moments in graphene can be induced from dopants, defects, or edges[66–68]. The possibility of long-range magnetic ordering has been predicted for randomly distributed point defects and grain boundaries[69, 70], and bilayer graphene was suggested to exhibit spontaneous many-body ferromagnetism[71]. However, experimental studies yielded contradictory results. Some observed room temperature ferromagnetic order[72–75], while other reported the absence of any sign of ferromagnetism in graphene from room temperature down to low temperature[76, 77]. Other 2D nanomaterials, such as layered transition metal dichalcogenides (TMDs), are promising for flexible and transparent electronics applications due to their sizeable band gaps within the 1–2 eV range[78–80]. Significant efforts have been used to prepare 2D dilute magnetic semiconductors by introducing magnetic atoms (e.g., Mn, Fe, Co, and Ni) into 2D TMD[81–85], and ferromagnetic ordering has been reported recently in TM-doped TMDs[85]. Nevertheless, lack of clear experimental evidence for ferromagnetic order formation in 2D layer hinders development of this nascent field.

The breakthrough of 2D magnetism came in 2017, ferromagnetism was demonstrated in van der Waals (vdW) crystals in the monolayer limit[86, 87]. In order to detect the ferromagnetic ordering of spins in a single atomic layer, a technique of much greater sensitivity than that provided by conventional magnetometers is required. To achieve the necessary level of sensitivity, a method called polar magneto-optical Kerr effect microscopy was used to determine the spatial extent of ferromagnetic order in their materials. With this powerful weapon, ferromagnetic order was demonstrated to remain intact in CrI_3 even in a single layer of the material (albeit with a suppressed Curie temperature of 45 K). A single layer of CrI_3 had a substantial remnant magnetization in the absence of a magnetic field, directed perpendicular to the plane of the lattice (Fig. 5). The magnetic system is therefore well described by the 2D Ising model[88]. In strong contrast to CrI_3, ultrathin layers of $Cr_2Ge_2Te_6$ had a highly suppressed Curie temperature in the 2D limit. Consistent with the Mermin–Wagner theorem[89], the ferromagnetic order was not present in a single layer of $Cr_2Ge_2Te_6$ even at 4.7 K, which was well described by the Heisenberg model[89]. Despite low Curie temperature, the progresses opened a door to explore low-dimentional magnetism and related phenomena, such as highly tunable *s*, *p*–*d* coupling via electrostatic gating, strain, and proximity effects in 2D system[90–93]. When it comes to practicality, however, achieving robust magnetic ordering at room temperature is still prerequisite.

3. Room temperature magnetic semiconductors with high transitional metal concentration

As a model system, (Ga,Mn)As had provided a good test bed to explore new physics and to design proof-of-concept spintronics devices. So people strived for a new material and transferred the experience with (Ga,Mn)As to it. It is noteworthy that it may be unrealistic if we are committed to find a room temperature dilute magnetic semiconductor with carrier-mediated ferromagnetism just like (Ga,Mn)As. To the best of our knowledge, nobody has demonstrated carrier-mediated ferromagnetism in a dilute magnetic semiconductor at room temperature. The problem is that the *s*, *p*–*d* exchange interaction mediated by free carriers is not large enough in such materials to align local spins ferromagnetically at room temperature, which precludes carrier-mediated ferromagnetism at room temperature in dilute system.

So we discuss a proposal to achieve thermally robust *s*, *p*–*d* interaction in semiconductors. According to the Anderson model[94, 95], the *s*, *p*–*d* exchange interaction energy depends on the concentration of magnetic ions and the density of states of conducting carriers. Consequently, the most direct way to realize thermally robust *s*, *p*–*d* coupling in semiconductors is to increase the concentration of magnetic dopants as well as carrier density. In fact, an ideal magnetic semiconductor should possess robust room temperature ferromagnetism that is primarily induced by a low-density carrier system, so that magnetic properties can be tuned over a wide range by doping or by gating[96]. To this end, the most critical step is to incorporate a higher concentration of magnetic ions into a semi-

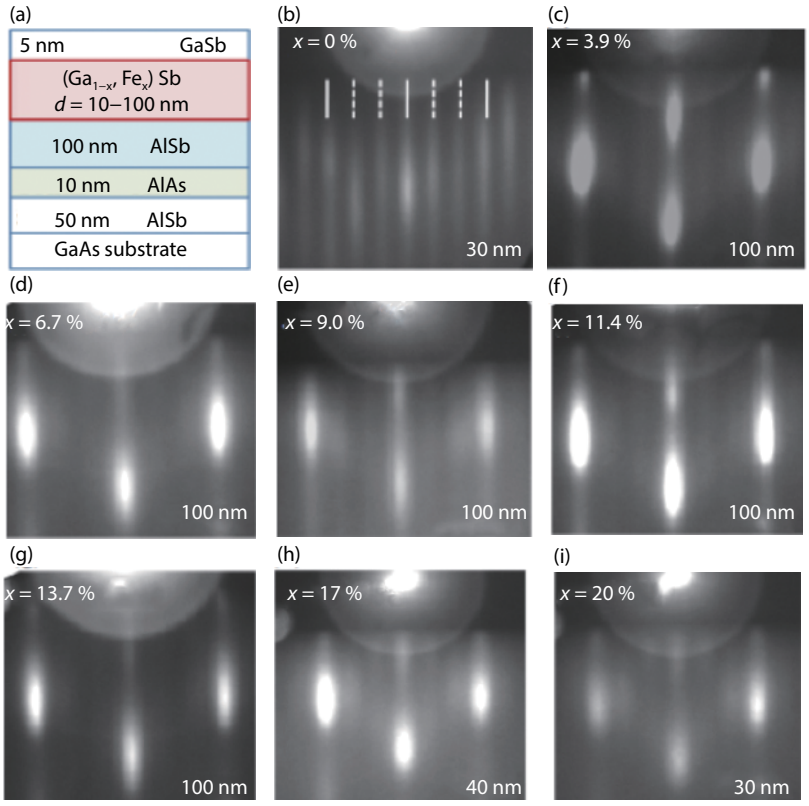

Fig. 6. (Color online) (a) Schematic fabrication of ($Ga_{1-x}Fe_x$) Sb thin films. (c)–(i) RHEED patterns taken along the $[\bar{1}10]$ azimuth after the MBE growth of the ($Ga_{1-x}Fe_x$) Sb layers for samples A–G (x = 3.9%–20%, thickness d = 30–100 nm). The RHEED pattern of an undoped GaSb sample is also shown as a reference in (b). Reprinted with permission from Ref. [99]. Copyright (2015) by AIP Publishing.

conductor by overcoming the obstacle represented by the low solid solubility of magnetic ions in conventional semiconductors. Furthermore, an extra high concentration (⩾ 30%) of magnetic ions must be introduced into the semiconductor matrix, substitutionally and uniformly. The high dopant concentration should persist in the crystal structure of the semiconductor host so that other important features of the host semiconductors are preserved. Although it sounds like a mission impossible, a few research activities have been directed to the development of magnetic semiconductors with high magnetic dopant concentration recently[97–108].

3.1. Single crystal magnetic semiconductors with high transitional metal concentration

Over the years, the endeavor for improving quality of materials has led to high control of the growth processes. In many cases, low solubility of magnetic elements can be overcame by low-temperature nonequilibrium molecular beam epitaxial (LT-MBE) growth. Recently, ($Ga_{1-x}Fe_x$) Sb (x = 3.9%–20%) thin films were successfully grown by LT-MBE[99]. Since Fe atoms are isoelectronic when doped in III–V semiconductors (i.e., they are neither acceptors nor donors), the ($Ga_{1-x}Fe_x$) Sb thin films maintain the zinc-blende crystal structure up to x = 20% (Fig. 6). The obtained T_C (230 K) of (Ga,Fe)Sb (x = 20%) is the highest in III–V magnetic semiconductors.

Another breakthrough was made in Co doped ZnO[101]. There are two common points between $Co_xZn_{1-x}O$ and ($Ga_{1-x}Fe_x$) Sb: the growth technologies are the same — LT-MBE; the dopants are both isoelectronic in host semiconductors. Single crystalline wurtzite $Co_xZn_{1-x}O$ epitaxial films with Co concentration x = 0.3–0.45 were grew under conditions far from thermodynamic equilibrium (Fig. 7). The films exhibit robust ferromagnetism and the magneto-optical Kerr effect at room temperature. The saturation magnetization reaches 265 emu/cm^3 at x = 0.45, which corresponds to the average magnetic moment of 1.5 μ_B per Co atom. Meanwhile, the remnant magnetization is 124 emu/cm^3. Nonetheless, spin-polarized transport behavior is not visible in those ferromagnetic films from room temperature down to 5 K[102]. By introducing Ga dopants to increase the carrier density, spin-polarized transport were observed at room temperature (Fig. 8)[103].

The concentration of Co in the films is high enough to exceed the threshold to percolate together and couple close-neighbor local spins to a parallel ground state. Therefore, the ferromagnetism is originated from ferromagnetic p–d coupling between O (2p) and Co (3d) orbitals in the presence of oxygen vacancies. In this regard, the films can be classified as a ferromagnetic insulator, owing to the localized 2p and 3d electrons lying at a deep level within the large band gap of ZnO. By contrast, electronic transport is dominated by s electrons. The polarization of conducting s electron can be very different from the local polarization determined by d electrons. If the s, p–d exchange coupling is very weak, then no spin polarized transport behavior can be observed, as shown in Fig. 9(a). In order to enhance the s, p–d exchange coupling, Ga was introduced to increase the conducting carrier density, because the s, p–d exchange interaction energy depends on the concentration of magnetic ions as well as the density of states of the conducting carrier. By increasing the conducting carrier concentration, the density of states near the Fermi level can be signific-

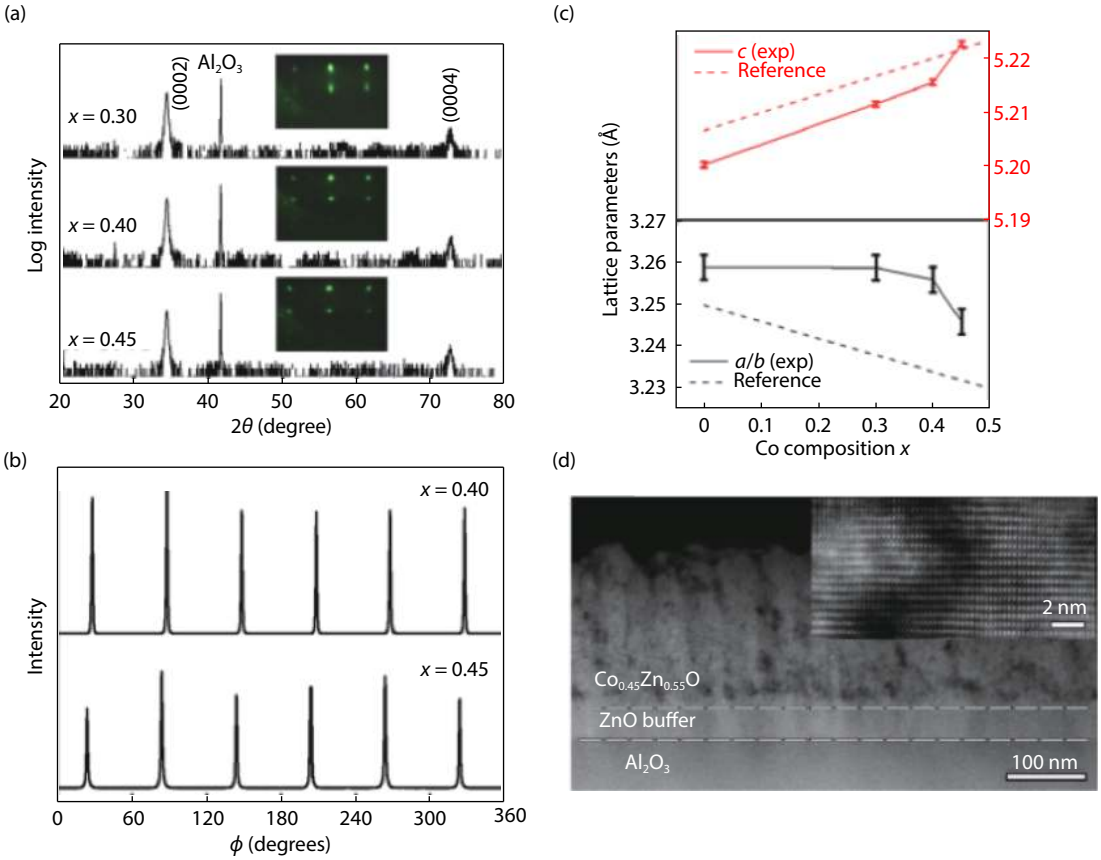

Fig. 7. (Color online) (a) XRD and corresponding RHEED patterns of the $Co_xZn_{1-x}O$ films with $x = 0.3$, 0.4, and 0.45, respectively. (b) $(10\bar{1}2)$ φ-scans of $Co_{0.4}Zn_{0.6}O$ and $Co_{0.45}Zn_{0.55}O$ films. (c) Experimentally (exp) determined lattice parameters of a/b and c for the $Co_xZn_{1-x}O$ films. The dashed lines are plotted with lattice parameters taken from the reference standards of bulk ZnO and wurtzite CoO[104]. (d) Crosssectional scanning TEM image of $Co_{0.45}Zn_{0.55}O$ film. The inset shows a high-resolution TEM image for the same film. Reprinted with permission from Ref. [101]. Copyright (2016) by AIP Publishing.

antly extended into the gap region, which gives rise to more overlapping between the delocalized electronic states (4*s*) and the localized impurity band (2*p* and 3*d*), as shown in Fig. 9(b). As a result, spin-polarized conducting carriers are created, and their density increases with carrier density, owing to the enhancement of *s*, *p*–*d* coupling between Ga (4*s*), O (2*p*), and Co (3*d*) orbitals.

3.2. Amorphous and/or nanocrystalline oxide magnetic semiconductors

However, the above dilute magnetic semiconductors and single crystal magnetic semiconductors with relatively high transitional metal concentration are largely limited by their stoichiometry, crystal structure and homogeneity. Beyond these limits, we propose that room temperature semiconductors with high spin-polarization may be realized by preparing amorphous, inhomogeneous and nonstoichiometric materials.

Nanocrystalline $Zn_{1-x}Co_xO$ and amorphous $Ti_{1-x}Co_xO_2$ magnetic semiconductor films with inhomogeneous composition on the subnanometer scale were prepared by sputtering under thermal nonequilibrium condition[105–108], where more than 50 at.% Co can be incorporated into the host ZnO and TiO_2. Fig. 10 shows the cross section micrograph, Co mapping, and chemical states of Co in $Ti_{1-x}Co_xO_2$ magnetic semiconductor films[106]. It can be seen that $Ti_{1-x}Co_xO_2$ magnetic semiconductor films are amorphous, and Co composition is inhomogeneous on the subnanometer scale. Moreover, the existence of Co metal clusters were excluded in $Ti_{1-x}Co_xO_2$ magnetic semiconductor, and the chemical states of Co element is close to Co^{2+}. Furthermore, the room temperature ferromagnetism with high magnetization was found in nanocrystalline $Zn_{1-x}Co_xO$ and amorphous $Ti_{1-x}Co_xO_2$ magnetic semiconductors. For example, the saturation magnetization of $Zn_{0.473}Co_{0.527}O$ magnetic semiconductor is as high as 581 emu/cm^3 at room temperature[105] and it gets to 524 emu/cm^3 at room temperature for $Ti_{0.24}Co_{0.76}O$ magnetic semiconductor[106].

One of the most important characters of magnetic semiconductors is the spin polarization. Therefore, a series of wide-band-gap ternary oxide ferromagnetic semiconductor films with high transition metal concentration were prepared to study the spin-polarized transport[107, 108]. It is found that the resistivity of these films can be changed up to four orders of magnitude by varying the composition or the concentration of the oxygen vacancies. The temperature dependence of the resistivity indicates that these magnetic semiconductors show spin dependent variable range hopping, which was companied by a large magnetoresistanc[107, 108]. A large negative magnetoresistance of 11% was found in $Zn_{0.473}Co_{0.527}O$ magnetic semiconductors at room temperature, and its value increased to 36% with decreasing temperature to 4.8 K[105]. The spin polarization ratio of these magnetic semiconductors can be obtained

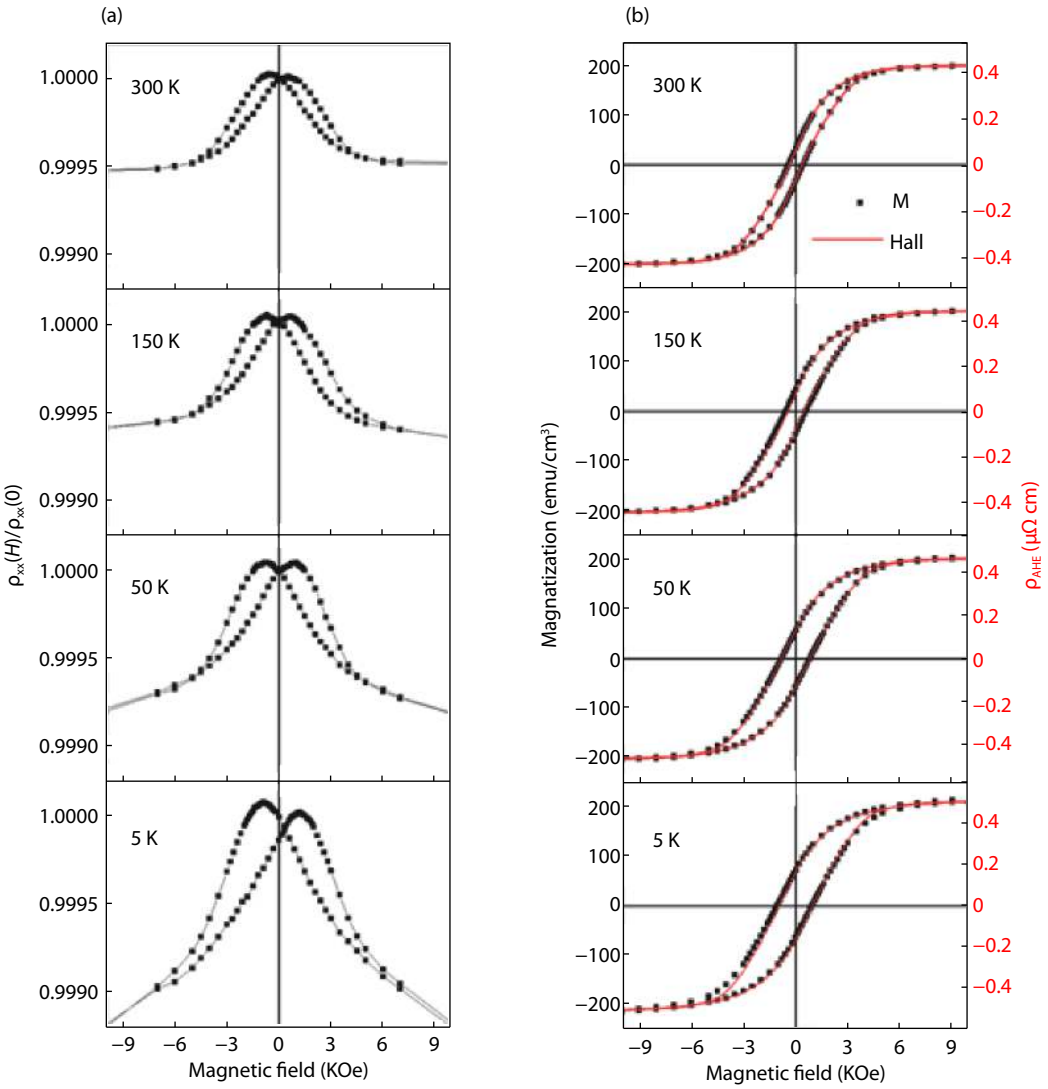

Fig. 8. (Color online) (a) Normalized MR and (b) anomalous Hall resistivity and corresponding M-H loops for the $Ga(Co_{0.4}Zn_{0.6})_{0.98}O$ film from room temperature down to 5 K. Reprinted with permission from Ref. [102]. Copyright (2017) by AIP Publishing.

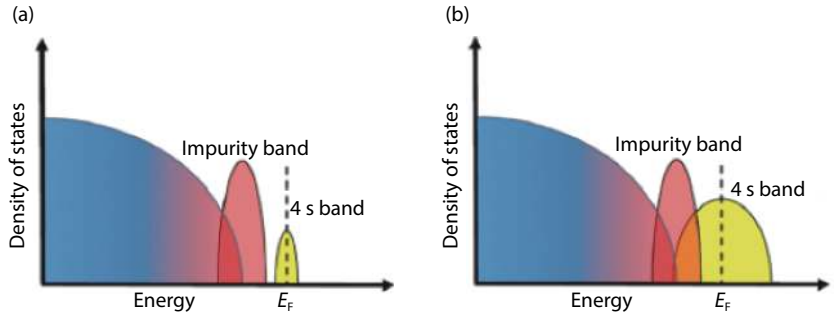

Fig. 9. (Color online) The schematic band diagrams as *s*, *p*-*d* coupling enhanced by increasing the density of *s* electrons. Dashed lines denote the Fermi level. Reprinted with permission from Ref. [102]. Copyright (2017) by AIP Publishing.

by fitting the spin dependent variable range hopping[108], as shown in Fig. 11. According to the fitting[108], the spin polarization ratio of the carriers is 36.1% in $Zn_{0.31}Co_{0.69}O_{1-v}$, and 21.9% in $Ti_{0.24}Co_{0.76}O_2$ magnetic semiconductor. Therefore, the wide gap oxide ferromagnetic semiconductors with controllable spin-polarized electrical transport are expected to have application in spintronics devices as a spin injection source.

4. Summary and outlook

It was long held that magnetic semiconductor research was confined to dilute magnetic compounds containing minute amounts of magnetic ions, which leads to a severe limit on its development. However, useful magnetic semiconductors, such as $Cd_{0.55}Mn_{0.45}Te$[16], may require high concentration of magnetic atoms. Fortunately, a great progress in the epi-

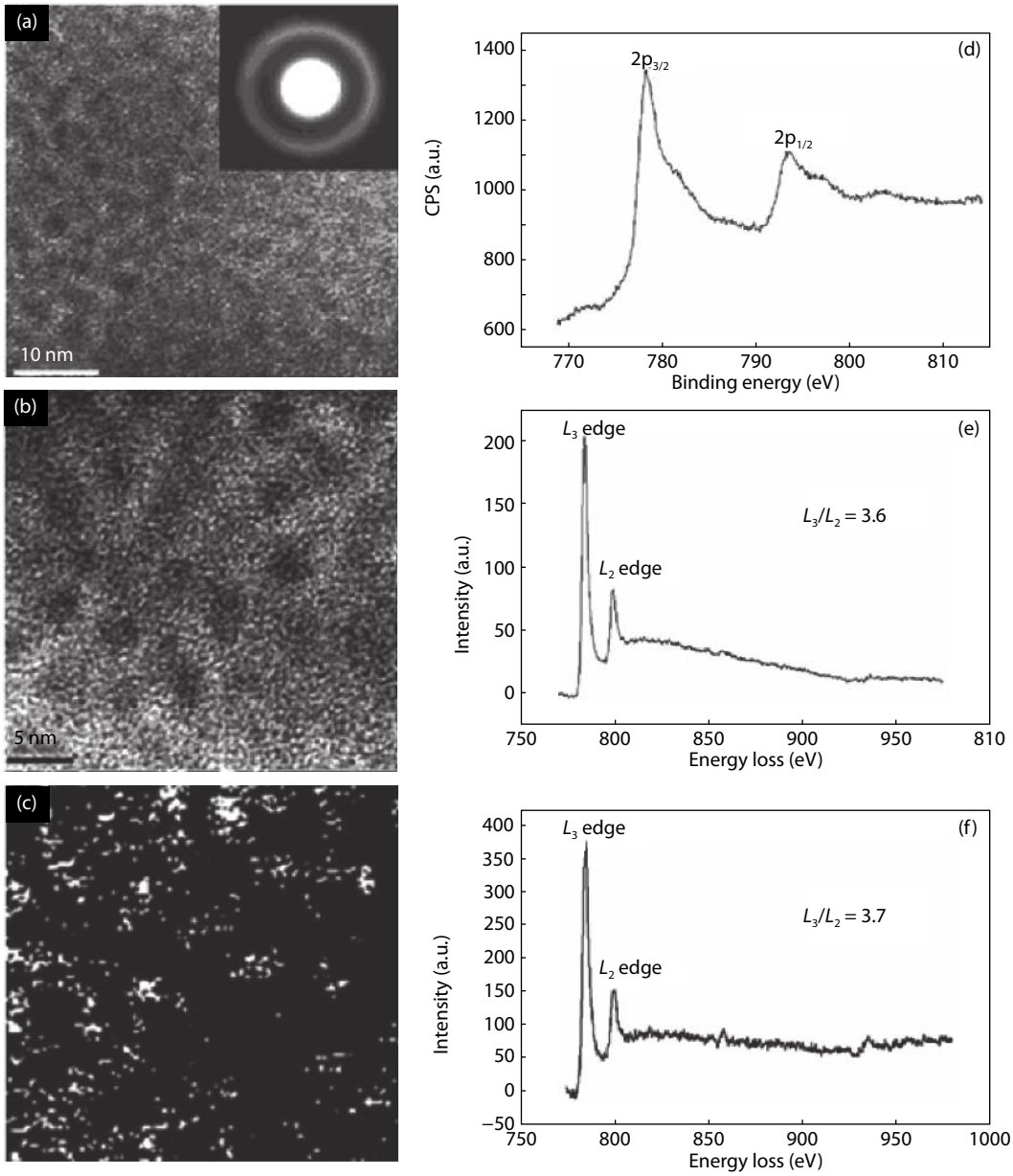

Fig. 10. (a) A low magnification micrograph of $Ti_{0.24}Co_{0.76}O_2$ films and the corresponding electron diffraction pattern in the inset. (b) The high resolution TEM image, and (c) the corresponding elemental mapping of Co. (d) XPS of Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks. (e) Electron energy-loss spectroscopy of $Ti_{0.24}Co_{0.76}O_2$ films. Reprinted with permission from Ref. [106]. Copyright (2006) by AIP Publishing.

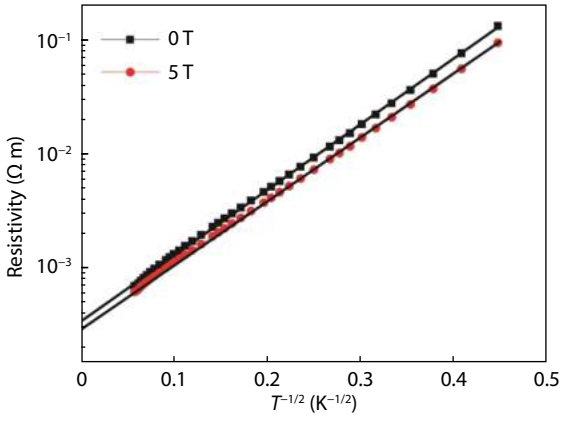

Fig. 11. (Color online) Resistivity in logarithmic scale versus $T^{-1/2}$ for the $Zn_{0.31}Co_{0.69}O_{1-v}$ magnetic semiconductors measured at zero and 5 T magnetic field. Reprinted with permission from Ref. [108]. Copyright (2010) by AIP Publishing.

taxy of semiconductor compounds has made it possible to introduce such a high concentration of dopants without ruining the crystal structure of semiconductor host. A tip of the iceberg for magnetic semiconductors with high magnetic dopants concentration has been emerged. We have a good reason to believe that the magnetic semiconductors with high concentration of magnetic elements will show us new surprise in the years to come.

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