Semiconductor Spintronics

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***Abstract*—We review recent progress made in the field of semiconductor spintronics, a branch of semiconductor electronics where both charge and spin degrees of freedom play an important role in realizing unique functionalities. We first describe the new spin-dependent phenomena found in semiconductors including carrier-induced ferromagnetism in III–V compounds, followed by an account of our current understanding of such spin-dependent phenomena. Then we summarize the challenges the semiconductor spintronics has to meet in order for it to be a success as "electronics."**

***Index Terms*—Ferromagnetic semiconductors, magnetooptic (MO) devices, magnetoresistive devices, quantum information, spin coherence.**

I. Introduction

THE SUCCESS of semiconductor electronics has been built on the charge degree of freedom of electrons in semiconductors. The spin degree of freedom, used in magnetic mass storage, has long been neglected in semiconductors because of the almost degenerate energies of the two spin states of electrons in semiconductors. However, because of the advances in semiconductor science and technology, the control and manipulation of the spin degree of freedom in semiconductors is becoming increasingly possible [1]–[3]. In addition, semiconductor technology has continuously reduced its working dimension to meet the demand for faster and denser integrated circuits. This leads us to a nanoscale dimension, where exchange interaction (a spin-dependent interaction) among carriers can no longer be ignored; like it or not, we will inevitably have to work with spin dependent interactions in semiconductors in the near future. Progress in magnetic imaging technologies has also started to reveal spin-dependent phenomena in nanoscale structures [4]. All these developments indicate that the time has come to explore, understand and utilize the spin-dependent phenomena in semiconductors. This may lead us to further increase the functionalities of existing devices and circuits like using the capability of mass storage and processing of information at the same time, and to realize quantum information technologies using spin as a qubit in solid state. This area of semiconductor electronics is called semiconductor spintronics, where both charge and spin degrees of freedom play an important and indispensable role in realizing functionalities.

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The latest semiconductor material technology offers a series of ferromagnetic semiconductors that are compatible with the existing nonmagnetic semiconductors (contain no magnetic element like Mn). Such compatibility allows us to integrate, in a single crystal structure, ferromagnetism with all the freedoms we are currently enjoying in semiconductors including heterostructures. These ferromagnetic semiconductor heterostructure can then be used to store information, amplify spin current, process information, and initialize and read-out spin quantum states. The combination of the advances in semiconductor material science, nanoscale physics and device technology, and integrated circuits, we should be able to polarize, inject, store, manipulate, and then detect spin information. To review current status, we summarized the new freedoms in spin manipulations in Section II. Section III describes our understanding of spin-dependent phenomena related to semiconductor spintronics. The prospect and challenges that we need to meet in the beginning of the 21st century are outlined in Section IV.

II. Semiconductor Spintronics Offers

A. Carrier-Induced Ferromagnetism

Recent developments in materials science and technology of semiconductors resulted in carrier-induced ferromagnetism in semiconductors that are currently used in transistors and lasers. Nonmagnetic semiconductors (i.e., containing no magnetic ions), such as GaAs, have been made magnetic by introducing a small amount of magnetic ions (like Mn). The ferromagnetism (alignment of spins of magnetic ions) is brought about by the carrier-mediated interaction among magnetic ions; without carriers no ferromagnetism occurs. This carrier-induced ferromagnetism in magnetic ion-doped semiconductors offers a variety of new controllability of semiconducting properties by magnetism and magnetism by semiconducting properties. When one changes carrier concentration by some external means, which can be done in semiconductors but not in metals, magnetism changes. This electronic control of magnetism has remained elusive but recently demonstrated in ferromagnetic semiconductors.

Fig. 1 shows the magnetic field dependence of Hall resistance (proportional to magnetization) of a field-effect transistor having a 5 nm thick p-type ferromagnetic $(In_{0.97}Mn_{0.03})As$ layer as a channel [5]. The measurement temperature is 22.5 K, in the vicinity of ferromagnetic transition temperature of the ferromagnetic semiconductor layer. When a gate voltage of

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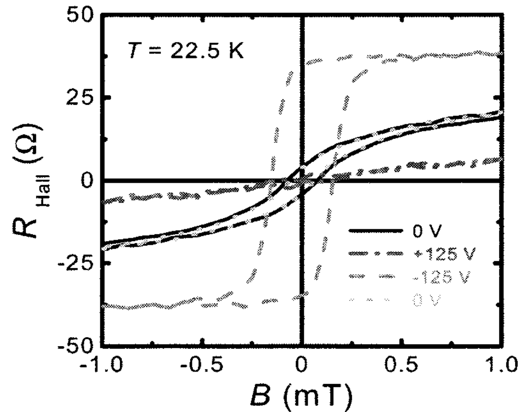

Fig. 1. Gate voltage dependence of Hall resistance in an (In,Mn)As FET structure close to the ferromagnetic transition temperature. When a gate voltage of $V_G = -125$ V is applied, hysteresis is clearly observed. On the other hand, when $V_G = +125$ V, the hysteresis disappears. This demonstrates that the applied field is able to switch the device between ferromagnetic and paramagnetic states [5].

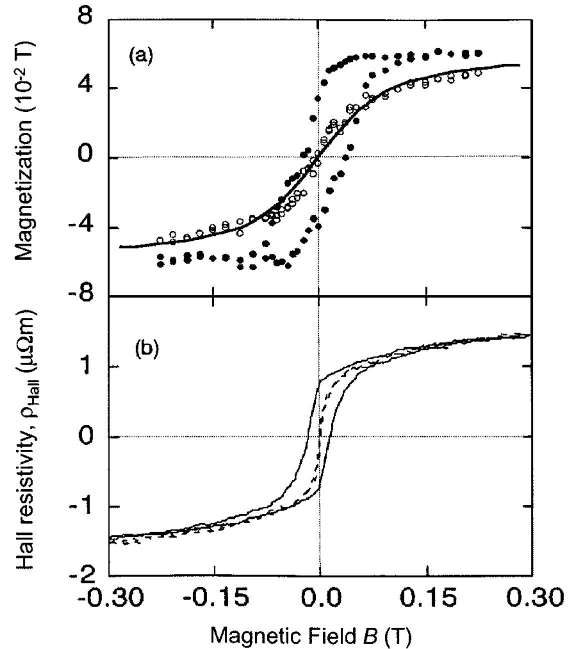

Fig. 2. (a) Magnetization curves and (b) Hall resistivity of a 12 nm thick $(In_{0.94}Mn_{0.06})As$ layer on a GaSb buffer layer at 5 K, before and after exposure to white light. The white and black circles in (a) correspond to the results obtained before and after exposure, respectively. The layer is paramagnetic before exposure, but after exposure the magnetization increases and it exhibits distinct hysteresis, indicating that it has become ferromagnetic (the theoretical curve is shown by the solid line). (b) Similar behavior appears in the Hall resistance—after exposure (solid line) it exhibits hysteresis that was not apparent before exposure (dashed line) [6].

$V_G = +125$ V is applied (electric field 1.6×10^6 V/cm), holes that mediate ferromagnetic interaction are partially depleted resulting in decrease of the channel magnetization and in the disappearance of hysteresis. Changing V_G to -125 V increases the channel magnetization and hysteresis becomes square. Virtually identical magnetization curve is restored upon returning to $V_G = 0$ V. This proof of concept demonstration shows that one can switch ferromagnetic phase on and off by applying external electric fields isothermally in a reversible way. Although the electric-field control of ferromagnetism is demonstrated at reduced temperatures, it opens up a range of new possibilities to control magneto-electronics devices.

Photo excitation also produces extra carriers in semiconductors. Koshihara *et al.* demonstrated that ferromagnetism can be induced by photogenerated carriers at low temperatures in heterostructures consisting of (In, Mn)As and nonmagnetic semiconductor GaSb [6]. This effect is illustrated in Fig. 2(a) and (b). Since the (In,Mn)As layer is only 12-nm thick, the incident light is mostly absorbed by the GaSb layer, where it produces electron–hole pairs which are then split by the internal electric field, causing the holes to accumulate in the (In,Mn)As layer at the surface side. The accumulated holes give rise to ferromagnetic transition when the initial hole density is tuned at the edge of the ferromagnetic–paramagnetic transition.

Optical control of magnetism has recently been reported by a number of researchers. Haneda *et al.* have grown GaAs with Fe particles, and have observed optically induced magnetization at room temperature [7]. Akinaga *et al.* have discovered optically-induced magnetoresistance effects at room temperature in a structure where nanoscale MnSb crystals are grown on a GaAs (111)B substrate and capped with GaAs [8]. Finally, Yuldashev *et al.* have reported enhanced positive magnetoresistance under light illumination in GaAs with nanoscale MnAs clusters [9].

B. Integration of Magnetooptical Effect

Faraday effect is an effect, in which the plane of polarized light transmitted through a magnetic material rotates in accordance with the sense of magnetization, and is currently being utilized to build optical isolators to allow stable and high bandwidth laser operation in optical fiber transmission systems. When excitation of erbium-doped fiber amplifier (EDFA) is carried out by the 980 nm wavelength light, the most efficient wavelength for excitation, one cannot employ conventional iron garnet based crystals for Faraday rotation because of the iron absorption in the wavelength region. Here, the only available solution is to use magnetic semiconductors. Semiconductor optical isolators based on a II–VI compound based magnetic semiconductor, (Cd,Mn)Te, have low absorption and a large Faraday rotation in the 980 nm wavelength region. Since (Cd,Mn)Te is paramagnetic, a magnetic field is applied to obtain Faraday rotation. A Verdet's constant of 0.05 deg/Oe·cm is currently achieved at 980 nm using (Cd,Mn,Hg)(Te,Se), with an overall insertion loss of 0.8 dB. This is the first commercially available semiconductor spintronic device [10]. When the bandwidths of network reach Gb/s at the end users, it becomes necessary to integrate lasers and isolators using the same semiconductors to realize high-performance low-cost devices. Magnetic semiconductors based on III–V compounds, such as (Ga,Mn)As, (In,Mn)As and their mixed crystals having a large Verdet's constant of a similar order to that of II–VI isolators near the band edge [11], may then be used to realize integration of compound semiconductor based lasers.

It is also possible to increase magneto-optical activity by introducing fine ferromagnetic particles into photonic crystals, thereby increasing relatively small interaction between particles and light. This has been demonstrated by dispersing ferromagnetic MnAs nanoscale particles in a thin film of GaAs [12],

which is a part of an one-dimensional semiconductor photonic crystal [13]. Model calculation has shown that the resulting Faraday effect is determined by the loss associated with the MnAs fine particles and the confinement of the electromagnetic field by the photonic crystal, and reduction of this loss is critical in realizing Faraday rotation required for isolators. In addition, the control of waveguide mode by varying the external magnetic field has been demonstrated in a (Cd,Mn)Te magneto-optical waveguide on GaAs substrates [14].

C. Ultra High-Sensitive Magnetic Sensor

Rapid increase in the magnetic recording density of hard disk drives demands highly sensitive magnetic-field sensors. Magnetic nanostructures, such as metallic multilayers and tunnel junctions, show giant magnetoresistance (MR) effect and have already been used as a read head in currently available hard disks [15] and [16]. All of them require nanometer order control of the constituent structures. For example, Giant MR (GMR) effect in metallic multilayers, so-called spin valve effect, was enhanced by using NiO layers with the nanometer thickness [17]. Tunnel MR (TMR) up to 50% at room temperature was reported in a ferromagnetic tunnel junction of Ta (5 nm)–NiFe (3 nm)–Cu (20 nm)–NiFe (3 nm)–IrMn (10 nm)–CoFe (4 nm)–Al (0.8 nm)–Al(0.8nm)oxide–CoFe (4 nm)–NiFe (20 nm)–Ta (5 nm) [18].

On the semiconductor front, the spin-dependent scattering similar to that observed in metallic magnetic structures has been reported. Fig. 3 shows an example of the spin-dependent scattering measured in a p-type (Ga,Mn)As–(Al,Ga)As–(Ga,Mn)As tri-layer structure [19]. The resistance increases when the two ferromagnetic layers have antiparallel magnetization. The antiparallel region appears as a stepped feature in the hysteresis loop of the magnetization curve obtained by the Hall measurements. In this region, the sheet resistance increases due to spin-dependent scattering. Although the magnetoresistance ratio is still small and is an low temperature effect, it is significant in that the spins do not relax even in the valence band, where a large spin orbit interaction is present. Minor loops measured in the same tri-layer structure showed the presence of ferromagnetic interlayer coupling. Results of polarized neutron reflectometry on (Ga,Mn)As–GaAs superlattices also showed the presence of the ferromagnetic interlayer coupling between (Ga,Mn)As layers, which may be mediated by holes [20]. A large TMR has also been observed in (Ga,Mn)As–AlAs–(Ga,Mn)As tri-layer structures [21] as shown in Fig. 4 [22]. In the stepped part where the magnetization is antiparallel, the tunneling resistance increases. When the AlAs film that constitutes the tunneling barrier is thin (1.6 nm), TMR ratio over 70% has been obtained. Although the high TMR ratio was achieved at 8 K, this large MR ratio suggests that the spin polarization has a high value of 50% in the ferromagnetic semiconductor, based on the Julliere's model [23].

Recent progress in molecular-beam epitaxy and vacuum metal bonding techniques has realized a spin-valve transistor, in which ferromagnetic metals and semiconductors have been integrated [24] and [25]. The transistor is a metal base transistor with a part of emitter and base being a spin-valve structure of ferromagnetic metals, where spin-polarized hot-electrons are injected from the ferromagnetic–metal emitter to the semiconductor collector, through the ferromagnetic–metal base. The magnetic-field response, defined as the change in the collector current normalized to the minimum value, reached 350% at room temperature [26]. Currently, the current transfer ratio is limited ($<10^{-5}$).

A unique magnetoresistance effect has been discovered in self-organized MnSb nanostructures grown by molecular beam epitaxy on a sulfur terminated GaAs surface. The magnetic field dependence of current–voltage characteristics show that an abrupt increase of current occurring at a certain threshold

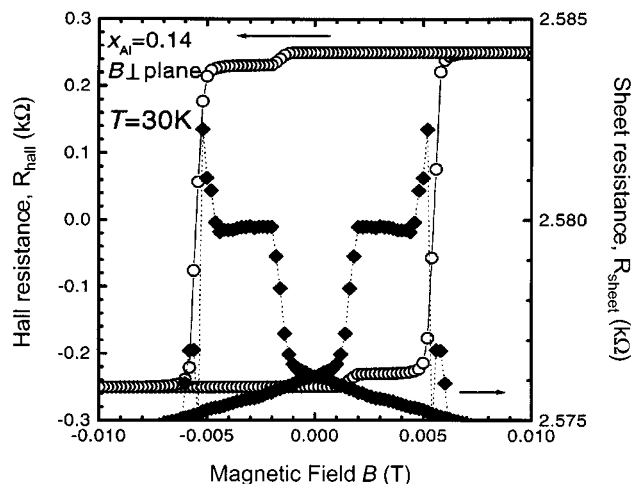

Fig. 3. The magnetic field dependence of Hall resistance (○) and sheet resistance (♦) in a (Ga,Mn)As–(Al,Ga)As–(Ga,Mn)As tri-layer structure. The magnetic field is applied perpendicular to the sample surface. By employing a Al composition 0.14 in the (Al,Ga)As, and by using a buffer layer of (In,Ga)As, the easy axis of magnetization is oriented perpendicular to the sample surface. In this way, by applying a magnetic field perpendicular to the sample surface, the anomalous Hall effect can be used to measure the parallel/antiparallel state of the magnetization. The region where the stepped part can be seen in the Hall resistance corresponds to the state where the magnetization is antiparallel, and in this region the sheet resistance is found to increase due to spin-dependent scattering [19].

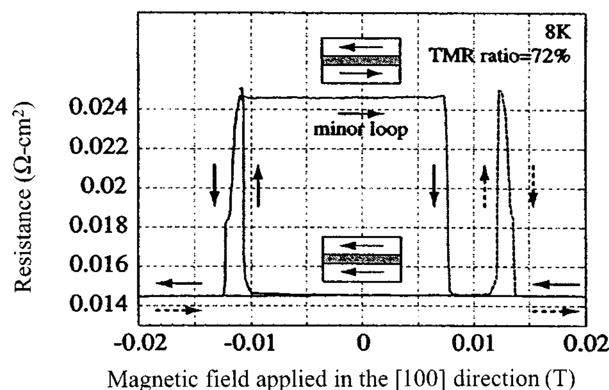

Fig. 4. Tunnel magnetoresistance effect in a (Ga,Mn)As–AlAs–(Ga,Mn)As tri-layer structure, measured at a temperature of 8 K. The solid and dotted arrows indicate positive and negative magnetic field sweeping directions, respectively. The (Ga,Mn)As layers are 50 nm thick, and the Mn composition in these layers are 0.04 and 0.033. The AlAs layer is 1.6 nm thick. Since the easy axis of magnetization lies within the plane of the sample, a magnetic field is applied parallel to the sample surface. When a magnetic field is applied along the [100] direction, a tunneling magnetoresistance effect of over 70% is observed, and when a magnetic field is applied along the [110] direction, this effect is approximately 30% [22].

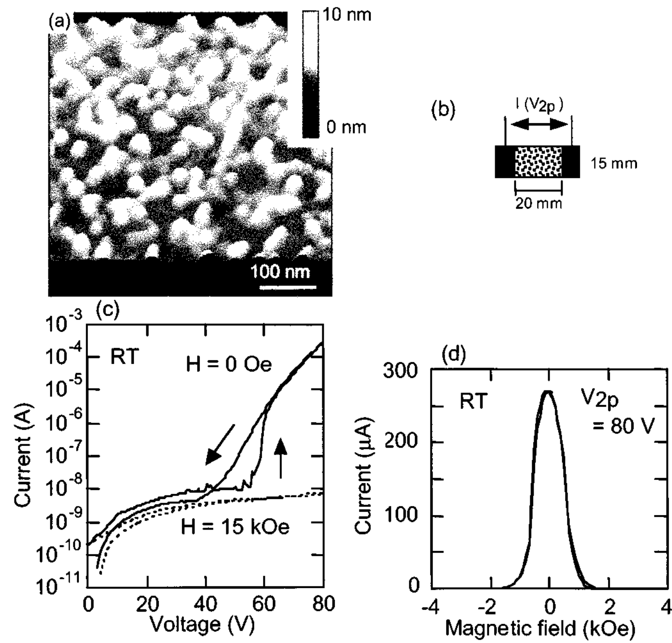

Fig. 5. (a) Typical atomic force microscopy image of a MnSb nanocluster grown on a sulfur terminated GaAs (001) substrate, then covered by an Sb cap layer of 3 nm. Note that each cluster is isolated from others. (b) Sample of the MnSb–GaAs granular film which was used for transport measurements. (c) Room-temperature I–V characteristics of the MnSb–GaAs granular film. The voltage scan rate was about 1 V/s. The curves measured under 0 and 15 kOe are indicated by solid and broken lines, respectively. The arrows beside the hysteresis indicate the voltage-scan direction. (d) Current-decrease by the applied magnetic field. The measurement was done at RT by applying the constant voltage of 80 V between two electrical contacts. The sweep rate of the magnetic field was kept at about 50 Oe/s. The decrease of the current is regarded as the positive MR effect. The resistance change derived from the switch effect becomes positive, and the MR ratio at the constant voltage of 80 V, defined as $\Delta R/R = (R(H) - R(0))/R(0)$, reaches 880% and 320 000% at $H = 1$ kOe and 2 kOe, respectively. The resistance is calculated as V_{2p}/I, where V_{2p} means the constant voltage applied to two electrical contacts.

voltage is highly magnetic-field sensitive and is suppressed upon applied magnetic fields. The increase of resistance reaches more than 10 000% at room temperature [27]; because of this large increase in resistance this device is named a magnetoresistive switch [28]. Fig. 5 shows a typical atomic force microscopy image of the granular film and the magnetic field dependence of the current change. The origin of the extremely huge magnetoresistance effect is currently explained by a magnetic-field sensitive avalanche breakdown. These properties strongly depend on the morphological condition of metal-nanoclusters and electronic properties of the GaAs surface. The physical understanding of the metal-nanocluster/semiconductor interface will be one of interesting topics in the research field of semiconductor surface science, and will give us a promising high-sensitive magnetic-field sensor. On related topics, a huge magnetoresistance effect was reported in InSb disk with a concentric Au inhomogeneity [29].

D. Spin Injection

Spin injection is one of the building block for a spintronic devices [30]–[32]. According to Schmidt *et al.*, spin injection into semiconductors from ferromagnetic metals, where carriers are partially spin-polarized, in diffusive regime is extremely inefficient due to the difference in the conductivity between the two involved materials; it is difficult to achieve efficient spin injection into semiconductors in a diffusive regime unless the degree of spin polarization in the ferromagnetic metal is close to 100% [33].

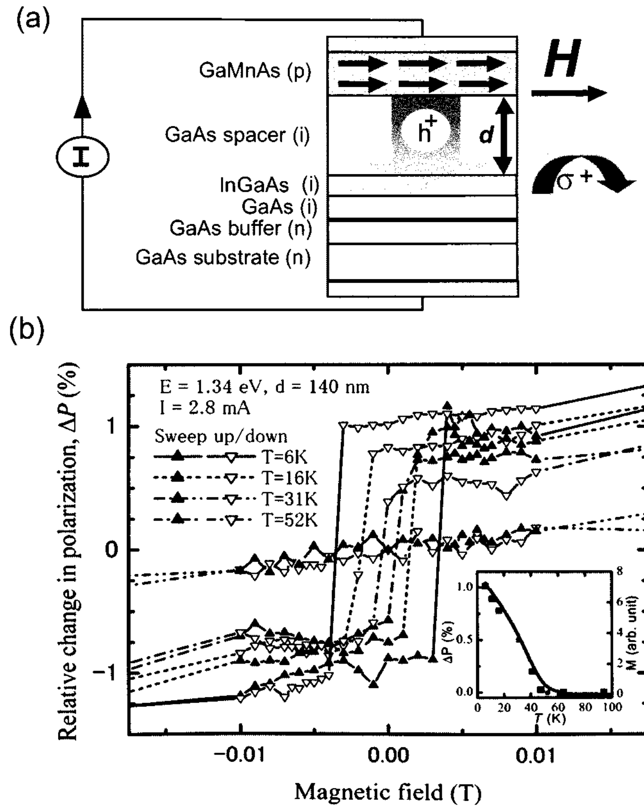

Fig. 6. Injection of spin-polarized holes into a light-emitting p–n diode using a ferromagnetic semiconductor (Ga,Mn)As [35]. (a) Sample structure. Spin-polarized holes h^+ travel through the nonmagnetic GaAs and recombine with spin-unpolarized electrons in the (In,Ga)As quantum well. I represents the current, and σ^+ represents circularly polarized light emitted from the edge of the quantum well. (b) Dependence of the polarization ΔP of the emitted light on the magnetic field B at each temperature. The solid and hollow symbols represent the degree of polarization when the magnetic field is swept in the positive and negative directions, respectively. The magnetic field was applied parallel with the easy axis of magnetization of the (Ga,Mn)As. The inset depicts the temperature dependence of the residual magnetization M in (Ga,Mn)As, where the degree of polarization of the zero magnetic field seen in the emitted light exhibits the same temperature dependence as the magnetization.

Since the conductivities of magnetic and nonmagnetic semiconductors are of the same order, and they can be grown epitaxially on each other, efficient spin injection is expected to occur between the two. Such spin injection has been realized using an LED structure with a p-type ferromagnetic semiconductor (Ga,Mn)As and n-type nonmagnetic semiconductor GaAs. Partially spin polarized holes are injected from the (Ga,Mn)As side into the nonmagnetic region and recombine with spin unpolarized electrons coming from the n-type side in a nonmagnetic quantum well made of (In,Ga)As, as shown in Fig. 6(a). The presence of spin polarization has been confirmed by measuring the polarization of the emitted light [34]–[36]. Fig. 6(b) shows the observed hysteresis in the degree of polarization of the emitted light at temperatures below the T_C of (Ga,Mn)As [35]. The use of ferromagnetic (Ga,Mn)As allows one to inject spins in the absence of magnetic fields; the magnetization direction of the ferromagnetic part can be read by the emitted light.

It is also possible to inject spin polarized electrons using band tunneling [37] and [38]. An efficient spin injection is achieved by the use of a paramagnetic semiconductor [34] and [39].

Rashba pointed out that the use of tunnel junction for spin injection can overcome the difficulty associated with the diffusive transport [40]. In the spin-valve transistor described above, the spin injection occurs as the nonequillibrium electrons (hot electrons) are injected into the semiconductor collector electrode. It has also been reported that by the use of a Schottky barrier, room temperature spin injection into an GaAs–(In,Ga)As LED structure is possible using an Fe electrode fabricated on the LED structure [41].

E. Control of Spin Polarization and Coherence

One of the great advantages of semiconductor spintronics is that one can control spin relaxation time and spin-coherence in a wide range, from picoseconds to milliseconds. Very fast spin relaxation can be used for optical gate switches, whereas long spin polarization opens up the possibility of utilizing spins as quantum bits for a quantum information processing.

Takeuchi *et al.* were the first to apply a circularly polarized pump probe method to the measurement of spin relaxation in semiconductor quantum wells. They have shown that the spin relaxation time of an AlGaAs–GaAs quantum well is 32 ps [42]. When spin polarization is generated in a quantum well by an external light, the absorption for right and left circularly polarized light differ as long as the polarization is present. By using this effect to extract optical signals only when spin polarization is present, very fast optically controlled gate switches can be constructed. In particular, in quantum wells containing different V atoms between barrier and well, such as InGaAs–InP quantum wells, the spin relaxation time is no more than a few picoseconds at room temperature [43].

When a magnetic field is applied perpendicular to the carrier spin, the spin undergoes Larmor precession about the field. The dynamics of such carrier spin coherence in semiconductors has been investigated by time-resolved optical measurements of the temporal development of the precession [44] and [45]. Kikkawa *et al.* have shown that the spin relaxation time can be extended to 100 ns in bulk n-GaAs with a doping density of 10^{16} cm^{-3} [46], and have demonstrated that spin-coherence can be transported over macroscopic scales of 100 μm as shown in Fig. 7 [47]. In addition, Malajovich *et al.* have shown that spin coherence can even be transported across a semiconductor junction with different band gaps and g values (different signs), such as GaAs–ZnSe heterojunctions [48] and [49]. It has been shown that electron spin coherence is maintained for periods of at least a few nanoseconds in n-type ZnCdSe–ZnSe quantum wells [50], in GaAs–AlGaAs (110) quantum wells [51], and in GaN [52]. These observations raise the possibility of application of confined electronic states to spin memory and manipulation [53] and [54].

F. Quantum Information Processing

One of the goals of semiconductor spintronics is to implement quantum information processing based on semiconductor devices using the two level nature and the long spin coherence

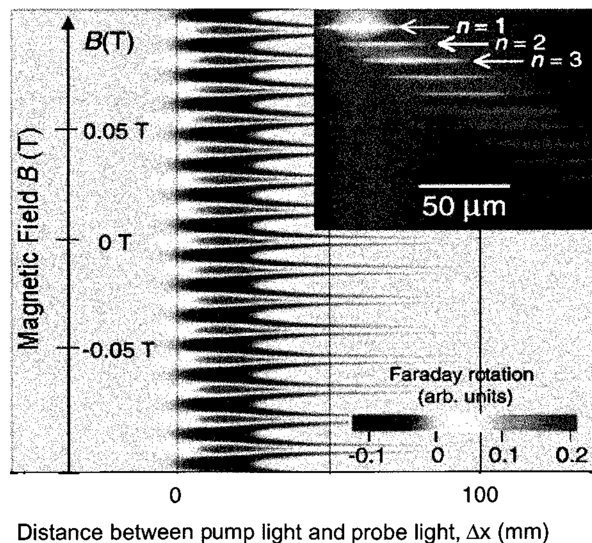

Fig. 7. Coherent transport of spin packets when an electric field is applied to n-GaAs [47], according to the time-resolved Faraday rotation measurements. The vertical axis shows the magnetic field B, and the horizontal axis shows the distance Δx between the pump light and the probe light. The measurements were made at 1.6 K. The excited electron spins precess about the magnetic field, and a large rotation angle (i.e., spin polarization) is observed when the period of this precession matches the period Δt of the excitation pulses. At time t, the spin phase of electrons excited by the nth pulse is given by $\omega(t + n\Delta t)$, where ω is the Larmor frequency. The inset shows the electron spin components generated at Δx, n periods previously (i.e., at $t - n\Delta t$), as determined by curve fitting.

times, of electron spins and nuclear spins. The use of semiconductors has various benefits for implementing quantum computers—not only are they solid state and suitable for large-scale integration, but they also allow dimensional freedom to be controlled by quantum confinement, and allow various characteristics to be controlled by external fields such as light and electric or magnetic fields.

A number of proposals have been made for quantum computers using a single-electron spin state in quantum dots as quantum bits, since it offers a two-level system close to the ideal case and it has relatively long coherence time [55]–[57]. To distinguish one quantum bit to be operated on from other quantum bits, the resonant frequency is shifted by, for example, applying a local magnetic field and this frequency is used for operation on the quantum bit. In a quantum computer proposed by Loss *et al.*, instead of subjecting the system to external electromagnetic fields, the temporal development of local exchange interactions between the target quantum dot and other neighboring quantum dots or ferromagnetic dots is introduced by a gate allowing the spin to be manipulated [55]. The use of solid-state (semiconductor) technology is, thus, advantageous in the way that it allows spin to be controlled electrically.

The majority isotope of silicon, ^{28}Si, has no nuclear spin. Therefore, any intentionally doped nuclear spin stands out and has a long relaxation time. Kane has proposed a Si-based quantum computer that uses a silicon MOS structure with a doped ^{31}P (nuclear spin 1/2), as shown in Fig. 8 [58]. The nuclear spin of ^{31}P acts as a quantum bit (qubit). It also acts as a donor that binds an electron. To manipulate the target's nuclear spin, a voltage is applied to a gate electrode located above the ^{31}P or between the neighboring ^{31}P. This way the hyperfine

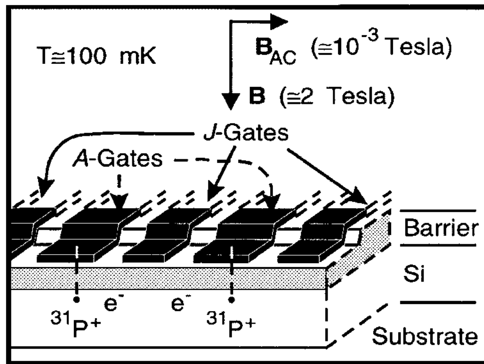

Fig. 8. A schematic illustration of a quantum computer proposed by Kane, in which nuclear spins $^{31}P^+$ embedded in a isotope-free ^{28}Si is used as a quantum bit [58]. The overlap between the electrons and the $^{31}P^+$ is controlled by the A gates, thereby varying the resonant frequency of the nuclear spin via hyperfine interaction. The J gates control the overlap of the electron wavefunctions between two neighboring $^{31}P^+$, allowing the manipulation of two quantum bits.

interactions, which are determined by the overlap of electron wave functions and nuclear spin, are controlled and the shift in nuclear magnetic resonance frequency is obtained [58]. To implement a quantum computer that uses nuclear spin, isotopic control of the host semiconductor crystal is essential. So far, useful experimental results such as greatly improved thermal conductivity have been obtained by controlling the isotopes [59] and [60]. Recently, Ito *et al.* succeeded in refining silicon to produce single crystals consisting of 99.924% ^{28}Si, which has much greater isotopic purity than natural silicon (where the abundance ratio of ^{28}Si is 92.2%) [61], and proposed an all silicon quantum computer [62].

Yablonovitch *et al.* have proposed an electron spin resonance (ESR) transistor based on Si–SiGe [63]. Here, a qubit is an electron spin state bound to a donor impurity in a quantum well consisting of two SiGe layers with different compositions. To manipulate spins, a gate voltage is applied so that the electron wavefunction is localized to one of the SiGe layers. Since Si and Ge have different g values, the resonant frequency of the localized electron spin can be controlled by shifting the position of the wavefunction by gating. This method is suitable for high-speed operation because the manipulation of quantum bits can be performed at the electron spin resonant frequency. Another advantage is that, since it uses Ge, the effective mass of electrons is smaller and the device dimensions can be increased to a size capable of being fabricated by existing micro-processing techniques (about 200 nm). Although the spin-orbit interaction in Ge is larger compared to that in Si, the electron spin coherence time is expected to be similar to that of Si (about 1 ms), which is long enough to allow computations to be performed provided that suitable error correction is applied.

To complete quantum information processing, one needs to read out a single nuclear spin or an electron spin state. Various methods have been proposed for doing this, such as spin filters using tunneling barriers of ferromagnetic material [64], and a method that involves using a single electron transistor (SET) to read out the spatial distribution of an electron wave function depending on the spin state [65]. The development of such device technologies is an important area for future work in the realization of quantum computers.

III. Magnetism and Spin-Dependent Phenomena in Semiconductors

This chapter offers a summary of the knowledge accumulated to date about the understanding of magnetism and spin-dependent phenomena in semiconductors. This is for those who are interested in the materials and physics behind the new functionalities.

A. Diluted Magnetic Semiconductors

Diluted magnetic semiconductors (DMS) are an alloy between a nonmagnetic semiconductor and a magnetic ion. They are called diluted as opposed to "concentrated" magnetic semiconductors such as EuO as in the latter the magnetic ion (Eu) is a part of its regular lattice, whereas in the former the magnetic ions partially substitute the nonmagnetic host atoms.

The beginning of the magnetic semiconductor study dates back to the late 1960s; at the time "concentrated" compounds were studied [66] and [67]. In the late 1970s through 1980s, the focus shifted toward DMSs based on II–VI compound semiconductors (and partially on IV–VI compounds) like (Cd,Mn)Te and (Zn,Mn)Te [68]. The preparation of II–VI compounds is relatively straightforward, mostly due to the compatibility of the valence of most of the transition metals (s^2) with that of group II element (s^2). Modern epitaxial thin film growth techniques (e.g., molecular beam epitaxy) are also available, allowing preparation of heterostructures and quantum nanostructures. II–VI based DMSs studied in the 1980s were either paramagnetic or spin-glass. These II–VI DMSs exhibit enhanced (sometimes called giant) magneto-optical effects under magnetic fields as a result of exchange interactions between carriers and the localized d electrons at magnetic ions, which is called the sp–d interaction as electrons and holes are made primarily from the s-orbital of the cation and the p-orbital of the anion of the host semiconductor, respectively. Doping of II–VI compounds, however, is often difficult and usually only one conduction type is available. This has been one of the major obstacles for the practical application of II–VI semiconductors as electronic and optoelectronic materials. Only very recently, became it possible to dope II–VI DMSs high enough to observe carrier-induced ferromagnetism. Ferromagnetism was also observed in a IV–VI DMS (Pb,Sn,Mn)Se at low temperatures, which was attributed to hole-mediated RKKY interaction [69].

B. Ferromagnetic III–V Semiconductors

Ferromagnetism observed in III–V DMSs introduces a new degree of freedom associated with the magnetic cooperative phenomena in the nonmagnetic semiconductor heterostructure system already in use in transistors and lasers. The compatibility with the existing heterostructures allows epitaxial integration of III–V magnetic/nonmagnetic layers and making it possible to explore new spin-dependent phenomena. Thus, the III–V magnetic/nonmagnetic system can be regarded as a prototypical system for future semiconductor spintronics, from which we can learn what can be done by the spin degree of freedom in semiconductors.

Nonmagnetic III–Vs have been made ferromagnetic by introduction of a few percent atomic concentration of magnetic

ions, which exceeds by far the equilibrium solubility in III–V semiconductors. In 1989, Munekata *et al.* used low-temperature molecular beam epitaxy (LT-MBE; deposition temperature approx. 250 °C) and succeeded in suppressing the surface segregation and formation of second phases, resulting in epitaxial growth of a metastable alloy of InAs and Mn, (In,Mn)As [70]. Three years later ferromagnetism was reported in p-type (In,Mn)As [71], and in 1996 the growth of (Ga,Mn)As [72]—a GaAs-based DMS—and ferromagnetic transitions in p-type (Ga,Mn)As were reported [73]. The highest ferromagnetic transition temperature T_C of (Ga,Mn)As obtained so far is 110 K (Mn concentration $x = 0.053$) [74]. Since (Ga,Mn)As can be epitaxially grown on a GaAs substrate, it is compatible with GaAs–(Al,Ga)As quantum structures, making it an indispensable material for the study of semiconductor spintronics [75]–[77].

1) Magnetic Properties: The easy axis of magnetization in (Ga,Mn)As grown on GaAs (001) planes is oriented within the plane due to lattice strain [73]. The lattice constant of (Ga,Ma)As is slightly larger than that of GaAs resulting in compressive strain in the epitaxial layer. This easy axis orientation can be made perpendicular to the epitaxial film when the sign of strain is reversed; this is possible by introduction of a lattice relaxed (In,Ga)As buffer layer with larger lattice constant than the (Ga,Mn)As layer grown on top of it [78]. Stripe shape magnetic domain has been observed, in accordance with the conventional theory, in (Ga,Mn)As with a perpendicular-to-the-plane easy axis [79].

The ferromagnetic transition temperature, T_C, can be determined in a number of ways: 1) the temperature dependence of remanent magnetization; 2) an Arrott plot ($M^2 - B/M$ plot) using the magnetic field dependence of the magnetization near the transition temperature; or 3) a Curie–Weiss plot of the magnetic susceptibility in the high-temperature paramagnetic region. These methods all produce almost the same T_C [81]. The relationship between T_C and x is $T_C = 2000x$ K up to around $x = 0.053$, and further increase of x results in decrease of T_C [74]. Increase of T_C up to 110 K by an thermal annealing was also demonstrated in (Ga,Mn)As without changing x [81] and [82]. The defect structure seems to play a role in this result, but the detail has not yet been fully understood. Efforts to increase T_C beyond 110 K in (Ga,Mn)As have so far been unsuccessful; the maximum T_C that (In,Mn)As exhibits is 50 K [83].

2) Mechanism Leading to Ferromagnetism: A model of carrier-induced ferromagnetism has been developed and shown to explain the experimentally observed features, especially T_C and its chemical trend. This mean field model assumes two spin subsystems, carrier spins and localized spins at magnetic ions, interacting through the exchange interaction (the sp–d interaction). Having a nonzero magnetization increases the free energy of the localized spin system, but reduces the energy of the carrier systems via spin-splitting of the bands (no energy gain if no carriers are present). The free energy penalty reduces as temperature is reduces and balances with the energy gain of the carrier system at $T = T_C$ [84]. This is known as the Zener ferromagnetism [85], which Zener himself later abandoned as in metals oscillatory interaction has to be taken into account due to high carrier concentration. Note that this Zener ferromagnetism is different from Zener's famous double exchange interaction.

Following the prescription, one can calculate T_C for a number of compounds. A 6 × 6 Luttinger–Kohn $\boldsymbol{k} \cdot \boldsymbol{p}$ Hamiltonian was used, where p–d interactions were taken into account, to calculate the carrier energy in the valence band. Only valence band was dealt with as (Ga,Mn)As is heavily p-type. For (Ga,Mn)As, the $\boldsymbol{k}\cdot\boldsymbol{p}$ parameters of GaAs and a value of $N_0\beta = -1.2$ eV were used. The latter was obtained from the core-level photoemission spectroscopy and modeling (N_0 is the density of cation sites, and β is the p–d exchange integral) [86]. An enhancement factor of 1.2 was included to account for the effect of carrier–carrier interaction [87]. The calculated T_C for (Ga,Mn)As, (In,Mn)As, and (Zn,Mn)Te all agree well with the experimental values. This model also explains the absence of ferromagnetism in n-type materials, which is because of the small exchange interaction in the conduction band; the s–d interaction is $N_0\alpha \sim 0.2$ eV (where α is the s–d exchange integral). The strain dependent easy axis of magnetization as well as the peculiar temperature dependence of magnetic circular dichroism in (Ga,Mn)As [88] are also explained by the model [89]. It has been pointed out, however, that other factors such as low energy spin-wave excitation and disorder must be considered [90] and [91].

By first principle electronic structure calculation, Akai showed that when holes are present, a half-metallic ferromagnetic state becomes stable in (In,Mn)As. He discussed the ferromagnetism being as a result of double exchange interactions caused by hopping of d holes [92]. First principle calculation also has shown that the ferromagnetic state is stable in a hypothetical zincblende GaAs–MnAs superlattice, where half-metallic state is predicted [93]. The double resonance mechanism has been proposed for the ferromagnetism of (Ga,Mn)As [94]. A large effort is currently being devoted to the understanding of ferromagnetism observed in transition metal doped semiconductors and we are witnessing a very rapid progresses in this theoretical area of research [95] and [96].

C. II–VI and Other Ferromagnetic Semiconductors

Advances in techniques for doping in II–VI semiconductors have made it possible to achieve carrier densities in excess of 10^{19} cm^{-3} [97]. Shortly after a theory of ferromagnetic transition based on p–d exchange interactions was put forward [98], ferromagnetism was observed below 1.8 K in modulation doped ($Cd_{0.975}Mn_{0.025}$)Te quantum well (8 nm, $p = 2 \times 10^{11}$ cm^{-2}) [99]. Ferromagnetism has also been observed in a thin film (500 nm thick) of ($Zn_{1-x}Mn_x$)Te and ($Be_{1-x}Mn_x$)Te (where $x \leq 0.1$) with $p = 10^{19}$–10^{20} cm^{-3} ($T_C < 3$ K) [100], [101], [102]. Room temperature ferromagnetism has been reported recently in a number of nonconventional magnetic semiconductors, 320 K in a II–IV–V_2 chalcopyrite ($Cd_{1-x}Mn_x$)GeP_2 [103], 290–380 K in (Zn,Co)O [104], room-temperature ferromagnetism in TiO_2:Co [105] and [106]. Sonoda *et al.* have recently succeeded in synthesizing (Ga,Mn)N showing ferromagnetic behavior at and beyond room temperature [107]; ferromagnetism in (Ga,Mn)N has been also reported by other groups [108] and [109]. The first observation of a ferromagnetic transition in a group-IV semiconductor has also been reported in Mn-doped Ge quite recently [110].

D. Nonmagnetic Semiconductors

Along with the developments of ferromagnetic semiconductors, numerous progresses in understanding and manipulating spin properties in nonmagnetic semiconductor structures have also been made over the last decade.

Carrier spin relaxation in semiconductors has been studied both theoretically and experimentally [111]. Time resolved laser spectroscopy of spin relaxation times in semiconductor structures have revealed that the major spin relaxation mechanisms include spin-orbit interactions originating from the lack of the inversion symmetry (the D'yakonov–Perel' effect), band mixing (the Elliott–Yafet effect), and electron–hole exchange interaction (the Bir–Aronov–Pikus effect) [111]. The relative importance among these mechanisms depends on material properties (the spin-orbit coupling and the fundamental band gap) and on parameters as dimension, temperature, kinetic energy, scattering time, and doping.

In quantum nanostructures, the degeneracy of light and heavy holes is lifted, and it is, thus, possible to achieve 100% spin-polarized carriers by resonant excitation of electron-heavy hole exciton with circularly polarized light. The introduction of quantum confinement also modifies mobility [112], symmetry [113]–[115], excitonic effects [116], locality [117], and doping [118], all resulting in modification of the spin relaxation processes. In GaAs, for example, the reported electron spin relaxation times are distributed over a wide range from a few picoseconds to several tens of nanoseconds [119]. In particular, the D'yakonov–Perel' effect dominant at room temperature depends strongly on the crystallographic orientation of the growth direction [115].

In quantum dots where the electron transport is dominated by the Coulomb blockade, it is possible to control the number of occupying electrons (even or odd) by varying the gate voltage [120]. In such few electron systems, spin (magnetism) plays a predominant role in the transport properties via exchange interaction. This behavior is expected to prove useful for functions such as spin filters and spin memories [121] and [122]. Exchange interactions between a quantum dot with a controlled spin state and an electrode (the Kondo effect) have also been observed [123] and [124].

To design and to implement solid-state quantum information processing that uses nuclear spin as a quantum bit, it is necessary to clarify the dynamics of interaction between electron spin and nuclear spin. So far, in semiconductors and its quantum structures, electron spin polarization have been measured to investigate the hyperfine interaction involving the Overhauser effect and the Hanle effect [111], [125], [126], and over the last few years more light has been shed on the dynamics of the Overhauser effect from the time-resolved pump–probe measurements [127]–[129].

IV. Semiconductor Spintronics Challenges

This final section summarizes a set of challenges that has to be met in order to materialize the advantages and opportunities offered by semiconductor spintronics. There are two directions for semiconductor spintronics; one is semiconductor magnetoelectronics, where magnetization direction is important, and the other is quantum information technology based on the spin degree of freedom in semiconductors. The two directions are closely related and cannot be separated at the early stage of research, but it is generally assumed that the magnetoelectronics would reach the application stage earlier than the quantum direction.

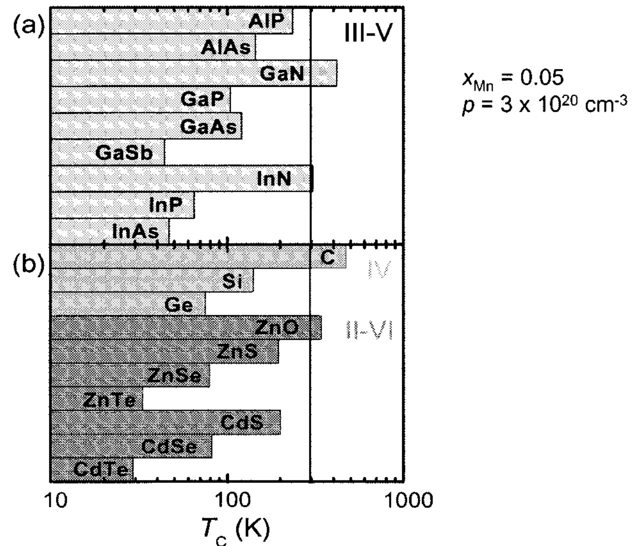

Fig. 9. Curie temperatures evaluated for various III–V (a) as well group IV and II–VI semiconducting compounds (b) containing 5% of Mn per cation (or 2.5% per atom) in 2+ charge state and 3.5×10^{20} holes per cm^3. Vertical thin line indicates room temperature [89].

A. High Ferromagnetic Transition Temperature

One of the most critical requirements for the use of ferromagnetic semiconductors is its ferromagnetic transition temperature T_C. It has to be well over room temperature for practical applications. According to the mean field model described in Section III, it is essential to increase both the density of magnetic atoms x and the hole density p; it is also necessary to satisfy $x > p$ [84] and [89]. The model predicts that if the hole density is fixed to $p = 3.5 \times 10^{20}$ cm^{-3} in (Ga,Mn)As (achieved in a sample with Mn concentration $x = 0.053$), T_C beyond room temperature can be achieved by increasing the Mn concentration above $x = 0.15$. The same model also shows that T_C higher than room temperature will be possible in wide-gap semiconductors such as GaN or ZnO, as shown in Fig. 9, if x and p similar to that of (Ga,Mn)As are realized. This is because of the light mass of the constituent elements and the small lattice constant, which result in a small spin-orbit interaction, a large effective carrier mass, and a large p–d exchange interaction ($N_0\beta \propto 1/a^3$, where a is the lattice constant), respectively [84] and [89].

The results of first-principle calculations also indicate that ferromagnetism is more stable in wide-band gap semiconductors. When ZnO is doped with a high concentration of a transition metal, doping with Mn results in antiferromagnetism (or ferromagnetism if simultaneously doped with holes), while V, Cr, Fe, Co, and Ni result in half-metallic ferromagnetism, and Ti and Cu result in paramagnetism [130]. For GaN, the calculation shows that the ferromagnetic state is stable when V, Cr, or

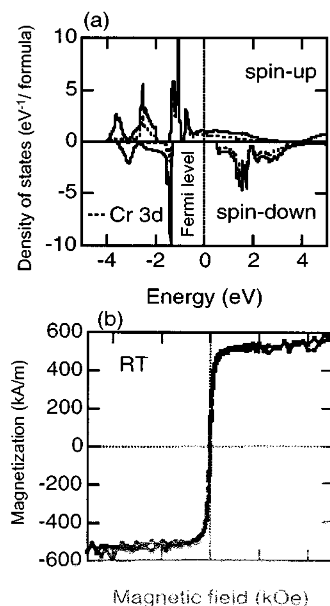

Fig. 10. (a) Density of states (DOS) in the ferromagnetic state of zincblende (zb) CrAs, predicted by *ab initio* calculations based on the local spin-density approximation. Broken lines denote the partial DOS for the Cr 3d orbital components, and the vertical dotted line indicates the position of the Fermi level. The calculation shows the half-metallic electronic band structure, i.e., the Fermi level lies in the energy band-gap of the minority-spin state (spin-down), while the energy-band of the majority-spin state (spin-up) is metallic. The total magnetic moment for zb–CrAs was calculated as 3 μ_B per formula unit, reflecting the half-metallic property. (b) Room-temperature magnetization hysteresis loop of the zb–CrAs thin film grown by molecular-beam epitaxy. The magnetic field was applied along the film plane. The saturation magnetization is 560 kA/m corresponding to about 3 μ_B per formula unit of CrAs, which agrees well with the theoretical prediction [133].

Mn are doped [131]. Experimental results showing room temperature ferromagnetism in a GaN–Mn alloy have been reported [107], [108], [109], although there still remain issues as to the extent of interaction between the semiconductor bands and the magnetic spins.

A new class of ferromagnets has been found to stabilize on semiconductor surfaces. These are zincblende CrAs and CrSb (see Fig. 10). These compounds were first designed by first-principle calculations that once the compound is stabilized in a zincblende form, the ferromagnetic phase is the most stable.[1] The calculation also predicts that zincblende CrAs is half metallic; 100% spin polarized in one spin direction [132]. The half-metallic ferromagnets, where the electronic band-structure of one spin-state is metallic while the other state semiconducting, are expected to enhance the spintronic device performances; it may be used for an efficient source of spin injection into semiconductors and for magnetic tunnel junctions exhibiting very large magnetoresistance. These surface-stabilized zincblende CrAs and CrSb thin films have been synthesized on GaAs substrates by molecular-beam epitaxy, and shown to exhibit ferromagnetism at room temperature [133] and [134]. Synergy between theoretical and experimental studies will become much more important to synthesize materials that are metastable and yet posses the desired properties. Thus, theoretical studies will be done not only to explain the observed phenomena but also to predict new functional materials.

[1]No Cr–As and Cr–Sb compounds showing a ferromagnetic properties at room temperature has been reported so far. Thermal equilibrium CrAs and CrSb compounds possess MnP and NiAs-type crystal structures. These compounds have been known to show a helimagnetic-paramagnetic transition at about 270 K and a antiferromagnetic transition at around 700 K, respectively [139].

B. Control of Ferromagnetism at Room Temperature

As described in Section II-A, the carrier-induced ferromagnetism was successfully achieved in field-effect transistor structures [5]. If this can be done at and above room temperature, it offers a method to change the magnetization direction at will, without applying large magnetic fields as one can switch on and off the ferromagnetism. This will lead us to a new form of storage device.

Spin-polarized current driven magnetization reversal in semiconductors should also be investigated. No established knowledge is available but the relatively large magnitude of exchange interaction (e.g., hole-spin exchange $N_0\beta = 1$ eV [86]) combined with the high spin polarization of injected spins is believed to be advantageous for reversing magnetization [22], [26], [34]–[36]. The spin polarized magnetization reversal is most useful for reversing small magnets, where the magnetic field required to flip the direction quickly increases as the dimension reduces due to the demagnetization field, and expected to have a profound impact on magnetic storage devices including magnetic random access memories [3].

C. Spin Amplification

Amplification is one of the things that are done best in semiconductors. If we can amplify spin polarization (or spin current) this will result in a highly sensitive magnetic field sensor. So far, the current transfer ratio of the reported spin-valve transistor is low. This low transfer ratio is inherent in all metal-base transistors due to the efficient energy relaxation mechanisms present in the metal base. If this difficulty is overcome by some means, however, then such a device is expected to completely change magnetoelectronics [135] and [136].

D. Single-Spin Detection and Operation

Majority of the proposals on semiconductor quantum computing using spins in semiconductors are based on single spin detection and operation. Neither of the two has been demonstrated to the accuracy and level required for quantum computing to date. One of the candidates is the magnetic resonance force microscopy, which has been predicted to reach single-spin sensitivity [137]. Electrical and optical quantum dot spectroscopy may also reach the sensitivity and controllability required for quantum information processing [120] and [138]. The first near term goal in this field is to demonstrate the single spin sensitivity and then the single spin operation, i.e., superposition of the two states. Next target would be the controlled-not operation between the two spin states in semiconductors; flip the second spin when the first spin is "down." Another approach to the same goal is to prepare a large number of the same set of spin states, on which measurements are done [62]. No such demonstration has been performed to date either.

V. Conclusion

We have attempted to review the recent progresses achieved in the field of semiconductor spintronics, where research are directed toward realizing functionalities by the use of both charge and spin degrees of freedom in semiconductors. Over the last 10 years, significant developments have been made in this field. We now have in our hand a number of prototypical systems ranging from ferromagnetic semiconductor heterostructures to long spatiotemporal spin coherence in nonmagnetic heterostructures. Working on these structures, we are learning, not only by theory but also by experiment, what are available to us in semiconductors by using the largely unexplored spin degree of freedom. The progress in room-temperature ferromagnetism in semiconductors will certainly make semiconductor magnetoelectronics possible and the long spin coherence time and length together with the various means of control and coupling to optics make spins in semiconductors a strong candidate for realizing future quantum information technology. Although semiconductor spintronics has begun to make progress, making it into real "electronics" requires a comprehensive and dynamic research and development program involving researchers from a broad spectrum of fields ranging from solid-state physics, crystal growth, magnetism, electrical and computer engineering, circuit design, and information science. Establishing links with researchers in other fields is becoming vitally important, and we invite you to join this exciting emerging field.

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