# Introduction to Dilute Magnetic Semiconductors

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(Dated: April 13, 2008)

This paper begins with a brief introduction to the field of spintronics and dilute magnetic semiconductor (DMS), the second part discusses in detail on three typical DMS materials–(Ga,Mn)As, (Ga,Mn)N and Transition metal doped oxide. Next mechanism of DMS ferromagnetism along with its magneto transport properties are discussed. Following that, an important sample preparation technique in DMS– Molecular Beam Epitaxial (MBE) – will be presented. Finally, conclusion and outlook are made towards the future study on DMS.

PACS numbers:

## I. BRIEF INTRODUCTION: DMS AND SPINTRONICS

Since late 1980s, people have noticed that in many semiconductor crystals, substitution of a transition metal element for a host element adds local magnetic moments to the systems's low-energy degrees of freedom[1, 2]. These doped materials are known as dilute magnetic semiconductors (DMSs), where usually a transition element is substituted on a small fraction, $x$, of a host semiconductor element sites. The study of DMS became flourished in recent ten years since high quality samples are available through experiment. It is widely believed that DMS are ideal material for spintronics. The following paragraph will explain what is spintronics and its applications.

The term "spintronics" stands for spin transition electronics. As well known today, integrated circuits and high-frequency devices, used for information processing and communications, have had great success through controlling the charge of electrons in semiconductors. Mass storage of information – indispensable for information technology – is carried out by magnetic recording (hard disks, magnetic disks...) using electronic spins in ferromagnetic materials. It is then quite natural to ask if both the charge and spin of electrons can be used at the same time to enhance the performance of devices. This is the main idea of spintronics, which is widely expected to be the future solution to downsize current microelectronic devices into size of even nanometers. The realization of functional spintronic devices requires materials with ferromagnetic ordering at operational temperatures compatible with existing semiconductor materials. Being a ferromagnetic semiconductor with favorable experimental properties, dilute magnetic semiconductors will promisingly suit this need.

## II. DMS MATERIALS

Two major criteria are considered to select the most promising materials for semiconductor spintronics. First, the ferromagnetism should be retained to practical temperatures namely room temperature. Second, it would be a major advantage if there were already an existing technology base for the material in other applications.

As early as late 1960 to early 1970, Oxide doped with $Eu^{2+}$[3] and spinel structured composite (for example, $ZnCr_2Se_4$[4]) are studied as magnetic semiconductors. However, structures of those composites are different from Si or GaAs, the crystals are very hard to produce in experiment, their low Curie temperature Tc (50K or lower), strong insulation and poor semiconducting transport property[5] further hampered their value in application.

Later on, studies have been spreaded on dilute magnetic semiconductors including transition metal (mainly Mn) doped II-VI, IV-VI and II-V compound semiconductors, typical examples are: II-VI: (Zn,Mn)Se, (Cd,Co)Se, (Hg,Fe)Te; IV-VI: (Sn,Mn)Te, (Pb,Mn)Te, (Pb,Eu)Te, *etc.* Mn doped II-VI semiconductors are especially focused on, typical materials are (Zn,Mn)Se *etc.*

For a long time, due to much lower solubility of magnetic ions in III-V semiconductors compared to II-VI semiconductors, along with its poor stability, not much studies are done on III-V DMSs. A breakthrough was made by using molecular beam epitaxy (MBE), a thin-film growth technique in vacuum that allows one to work far from equilibrium. Using MBE technique, Munekata etc. successfully made III-V material InMnAs, and ferromagnetism was observed in p type InMnAs[2]. Based on the work above, in 1996, Ohno etc. made the first Mn doped dilute magnetic semiconductor (Ga,Mn)As[6]. This material was grown as a $Ga_{1-x}Mn_xAs(x = 0.015 \sim 0.017)$ thin film on a semi-insulated GaAs(001) substrate. The fraction of Mn ions in the sample was as high as $(3 \sim 7) \times 10^{20}\text{cm}^{-1}$, which was far higher than the solubility of GaAs in thermal equilibrium. Furthermore, because that (Ga,Mn)As were grown on GaAs film, its crystal structure has a good similarity to GaAs. Due to its remarkable properties, (Ga,Mn)As attracted a lot of

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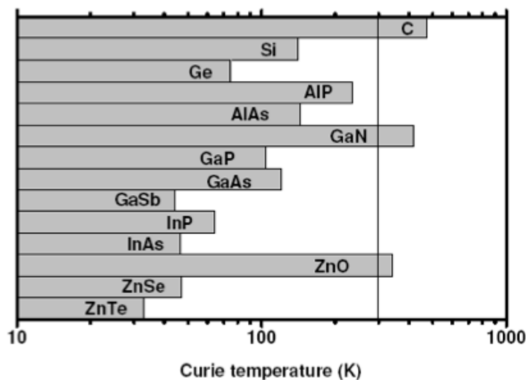


FIG. 1: Computed values of Curie temperatures $T_c$ for various p-type semiconductors containing 5% of Mn per cation (2.5% per atom) and $3.5 \times 10^{20}$ holes per $cm^3$[12, 13]

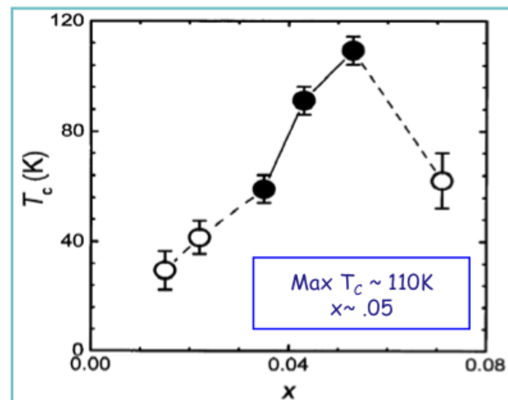


FIG. 2: Curie temperature vs. Mn concentration for DMS (Ga,Mn)As[14]

interests on DMS studies as soon as it appeared in the experiment.

Typically the observed curie temperature of DMS is mostly below 50K, the highest $T_c$ on (Ga,Mn)As is only 110K. So an important step for DMS to be applied in reality is to improve its $T_c$. Many new DMS materials are discovered in recent research, for example Mn doped $CdGeP_2$[7], CrAs[8], $(Ti,Co)O_2$[9], (Zn,Co)O[10] and (Zn,Ni)O[11], etc. In 2000, Dietl explained curie temperature in $Ga_{1-x}Mn_xAs$ and $Zn_{1-x}Mn_xTe$ theoretically using Zener Model, and predicted the existence of room temperature DMSs, as in Fig. 1[12].

Recent research are mainly focused on the following DMS materials:

### A. (Ga,Mn)As

GaAs are already in use in a wide variety of electronic equipment in the form of electronic and optoelectronic devices, including cellular phones, compact disks, and in many other applications. Therefore, the introduction of magnetic semiconductors based on GaAs opens up the possibility of using a variety of magnetic phenomena not present in conventional nonmagnetic GaAs material in the optical and electrical devices already established.

In 1996, Ohno firstly used MBE technique to produce $Ga_{1-x}Mn_xAs$ thin film with a largely enhanced solubility of the order of $10^{20}cm^{-1}$. Through study of its magnetic transportation, it was found that the Curie temperature varied as a function of doping factor $x$, and its behavior satisfied $T_c = 2000x \pm 10K$[6]. Later F. Matsukura etc discovered that the Curie temperature of (Ga,Mn)As reached its highest 110K when $x = 0.05$, as shown in Fig. 2. When Mn concentration was reduced, Curie temperature $T_c$ would also decrease, when Mn concentration $x$ went below 0.005, ferromagnetism would disappear[14]. Moreover, as Mn concentration in (Ga,Mn)As increases, the transportation properties experienced series of changes, i.e., non-metal to metal and again to non-metal[15].

Study of origin of ferromagnetism in (Ga,Mn)As has always attracted lots of attentions. H. Ohno etc believes that it is hole charges who lead to ferromagnetism in (Ga,Mn)As[6]. They discovered that the number of Mn ions in (Ga,Mn)As is of the same order compared to those of hole charges, which supported their opinion. Nowadays, it is still not fully understood the reason of ferromagnetism in (Ga,Mn)As. Based on the study of (Ga,Mn)As, Other DMS materials with even higher Curie temperature has been discovered, for example, (Ga,Mn)N, Co: $TiO_2$ etc. However, they are all not as good as (Ga,Mn)As in terms of experimental capability and compatibility with current semiconductor industry. Till now, (Ga,Mn)As is the most promising DMS material in practice.

### B. (Ga,Mn)N

In Dietl's theoretical calculation, Curie temperature of Mn doped GaN is the highest among various semiconducting compound, thus (Ga,Mn)N has a wide spread interests in researchers. In 2001, Zajat etc made highly doped (Ga,Mn)N using an ammonothermal method, which has paramagnetism, and they believe that p type (Ga,Mn)N can gain ferromagnetism[16]. In the same year, Reed etc reported that they grew a 2$\mu$m thick single crystal on (0001) sapphire substrates using metal organic chemical vapor deposition (MOCVD) method, and then a laser deposition technique was used to deposit Mn on the Nitride samples[17]. Mn doping was achieved by deposition and annealing at different temperatures ranging from 250–800°C. The experiment implies that Curie temperature of grown samples will depend on growing and annealing conditions, which are between 220∼370K[18]. Theodoropoulou etc used a similar method and achieved Mn doped P type GaN, with a high dose of 3∼5%. The observed Curie temperature is lower than theoretical predictions, the author believes it is due to lower concentra-

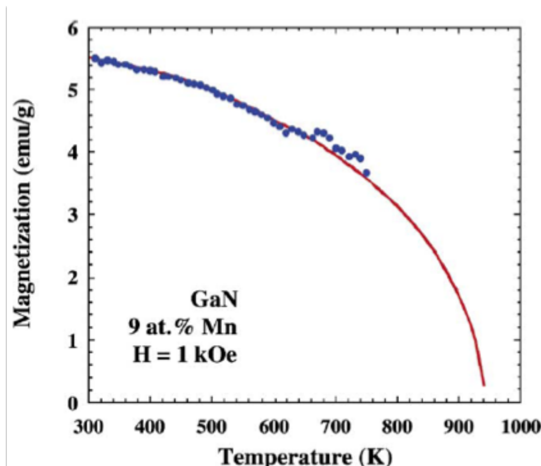


FIG. 3: Magnetization vs. temperature for (Ga,Mn)N sample grown by MBE with ∼9 at.% Mn. The extrapolation of the curve is based on a mean-field approximation[20, 21]

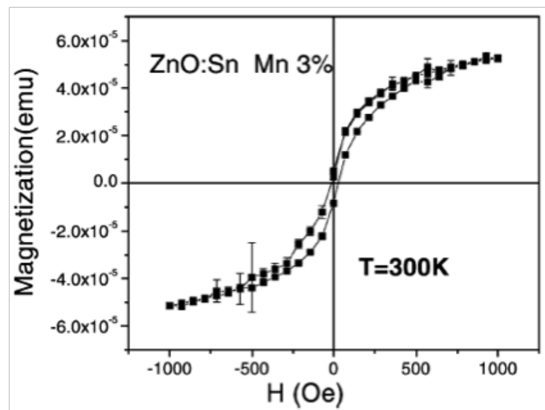


FIG. 4: Room temperature hysteresis for bulk ZnO(Sn) implanted with 3 at.% Mn[1]

tion of holes[19]. Fig. 3 shows the temperature dependence of the magnetization for a sample with 9 at.% Mn, yielding an estimated $T_c$ of 940K using a mean-field approximation.

### C. Transition metal doped oxide

Semiconducting oxide has wide energy gap, good light transmission, can be doped to get n type semiconductor. These preferable properties made them widely used in practice[22]. Thus, there are also many ongoing research in oxide DMS, which is now mainly focused on transition metal doped ZnO and $TiO_2$ materials.

In 1999, Fukumura etc produced Mn doped ZnO thin film using Pulsed Laser Deposition (PLD). ZnO and $Mn_3O_4$ are heated at 900°C and mixed with a certain percentage for 12 hours. Concentration of electron carriers is of the order of $10^{19}\text{cm}^{-3}$. In the grown sample $Zn_{1-x}Mn_xO$, considerable magnetoresistance is observed at low temperatures[23]. Two years later, Sato etc proved theoretically that Mn, Fe, Co and Ni doped ZnO DMSs may have stable ferromagnetism[24]. Ueda etc reported ferromagnetism in Co doped ZnO thin film made by PLD method, but only with a low repeatability (about 10%)[10]. Jin et al produced Co doped ZnO using laser molecular-beam epitaxy (MBE), but no ferromagnetism was observed[25]. Cho et al produced CoFe doped ZnO – $[Zn_{1-x}(Co_{0.5}Fe_{0.5})_xO]$ thin film – using reactive magnetron co-sputtering and fast annealing. The film sample achieved has $x \geq 0.15$, and has the same crystal structure of ZnO. It is indicated that annealing can greatly enhance self magnetization and carrier concentration of samples, thus increase Curie temperature to even room temperature[26]. Fig. 4 shows the magnetization behavior at 300K for a Sn-doped ZnO sample implanted with 3 at.% Mn, clearly indicating ferromagnetism[1].

Co doped $TiO_2$ is also observed to have room temperature ferromagnetism. In 2001, Matsumoto reported that Co:$TiO_2$ (doped Co below 5%) film made by PLD displays room temperature ferromagnetism, and its Curie temperature $T_c > 400K$[9]. Another experiment achieved greater than 300K Curie temperatue in the same material but made by oxygen plasma assisted molecular beam epitaxy (OPA-MBE)[27]. Later on, Co doped $TiO_2$ film with high Curie temperature were also achieved by several other experiment on various substrates[28–30].

Mn doped $SnO_2$ is predicted as another DMS. H. Kimura discovered magnetoresistance in Mn doped $SnO_2$ at low temperature 5K[31].

## III. MOLECULAR BEAM EPITAXIAL TECHNIQUE

The major obstacle in making III-V semiconductors magnetic has been the low solubility of magnetic elements (such as Mn) in the compounds. Because the magnetic effects are roughly proportional to the concentration of the magnetic ions, one would not expect a major change in properties with limited solubility of magnetic impurities, of the order of $10^{18}\text{cm}^{-3}$ or less.

A breakthrough was made by using molecular beam epitaxy (MBE), a thin-film growth technique in vacuum that allows one to work far from equilibrium. When a high concentration of magnetic elements is introduced in excess of the solubility limit, formation of the second phase occurs if conditions are near equilibrium. However, when crystal is grown at low temperature by MBE, there is not enough thermal energy available to form the second phase, and yet there still exists a local potential landscape that allows epitaxial growth of a single-crystal alloy. The effort to grow new III-V based DMSs by low-temperature MBE was rewarded with successful epitaxial growth of uniform (In,Mn)As films on GaAs substrates in 1989, where partial ferromagnetic order was found, and ferromagnetic (Ga,Mn)As in 1996.

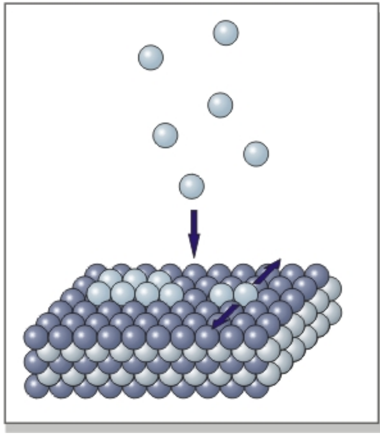

FIG. 5: Material deposition process in MBE[32].

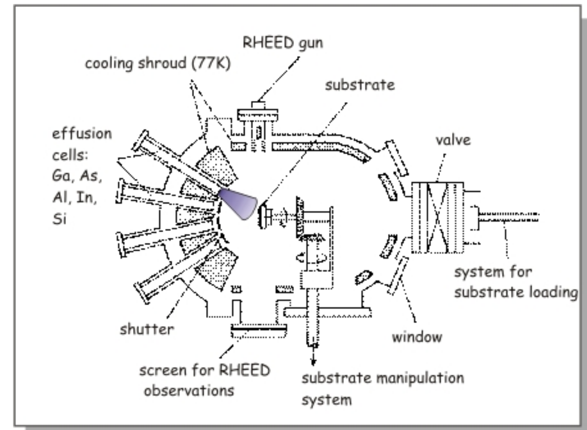


FIG. 6: Illustration of a MBE construction[32].

In a ultra-high vacuum, a beam of atoms or, more general, a beam of molecules is directed towards a crystalline substrate such that the atoms or molecules stick at the substrates surface forming a new layer of deposited material, as shown in Fig. 5. The difference between MBE and other material deposition methods as e.g. thermal vacuum evaporation is as follows. MBE does not only deposit material like it is done by conventional evaporation techniques, but using the very low rates of impinging atoms, migration on the surface and subsequent surface reactions ensure the controlled epitaxial growth of a new layer. Simply spoken: Every atom reaching the surface of the heated substrate has enough time to migrate around and find his place to build up a new crystal lattice. With lots of physics applied, chemistry and engineering work done since beginning MBE in the late 60s and the early 70s to reach state of the art MBE.

The typical construction of a MBE is shown in Fig. 6. At the left hand side there are the effusion cells to provide the molecular beam for either the bulk constituents or the dopants. These cells can be thermal evaporation cells (Knudsen cells), cells for gaseous media or plasma sources as well. In front of them is a shutter, this means a plate which could be brought into the beam for switching the beam on and off. Opposite to the cells and the shutters is the substrate, mounted on a heatable and rotatable substrate holder.

The whole system is in ultra-high vacuum environment to guarantee formation of a molecular beam (without vacuum, the atoms or molecules leaving the effusion cells will be scattered at residual gas molecules and never form a beam directed towards substrate) and purity and therefore quality of the grown layer. Often there are instruments for in-situ analysis like RHEED attached to the growth chamber. A cryopanel around the sample and the cells absorbs residual gases and provides a clean substrate environment.

## IV. MAGNETIC MECHANISM AND PHYSICAL PROPERTIES

### A. Exchange interaction

When magnetic ions are doped into semiconductors, they will substitute part of positive ions, their local spin momentum has strong spin-spin exchange interaction with carriers, which further will lead to different behavior of charge carriers, thus make DMS different from normal semiconductors. Spin-spin exchange interaction is the key point through which various magnetic moments are formed and DMS materials differ from non-magnetic materials. In DMS, exchange interaction include interactions between s electrons in conducting band, p electrons in valence band and d electrons from magnetic ions (sp-d exchange interaction) and interactions between d electrons from magnetic ions(d-d exchange interaction)[33].

Soaleck etc indicated that it is the distance between nearest $Mn^{2+}$ ions that determines the exchange integral factor after analyzed many experimental results. Experiments show that exchange interaction between magnetic ions is due to superexchange mediated by negative ions in distorted crystal lattice[33].

Fig. 7 shows the operative mechanisms for magnetic ordering in Mn doped DMS (Ga,Mn)As. There are two basic approaches to understand the magnetic properties of dilute magnetic semiconductors. The first one is based on mean field theory which originates in the model of Zener[34]. The theories that fall into this general model implicitly assume that the dilute magnetic semiconductor is a more-or-less random alloy, in another word, the doping atoms will substitute randomly for the lattice constituents. Within these theories, there are differences in how the free carriers are assumed to interact, as shown in Fig. 8. The second class of approaches suggests that the magnetic atoms form small (a few atoms) clusters that produce the observed ferromagnetism[35].

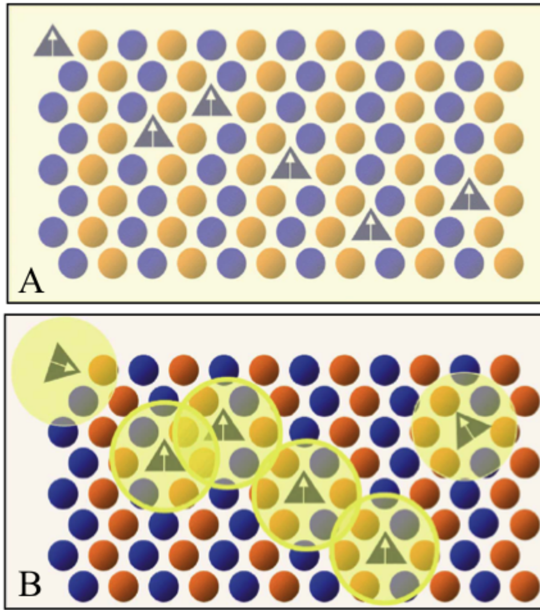


FIG. 7: Illustration of carrier mediated ferromagnetism in dilute magnetic semiconductor (Ga,Mn)As. $Mn^{2+}$ ions sit on trivalent Ga sites (triangles), and therefore act as electron acceptors (providing holes) as well as producing a magnetic moment (arrows).
(A) The holes are thought to mediate ferromagnetic coupling between the magnetic $Mn^{2+}$ ions.
(B) Below certain temperatures, a percolation network is formed in which clusters of the holes are delocalized and hop from site to site, which is an effective mechanism for aligning Mn moments within the cluster network.

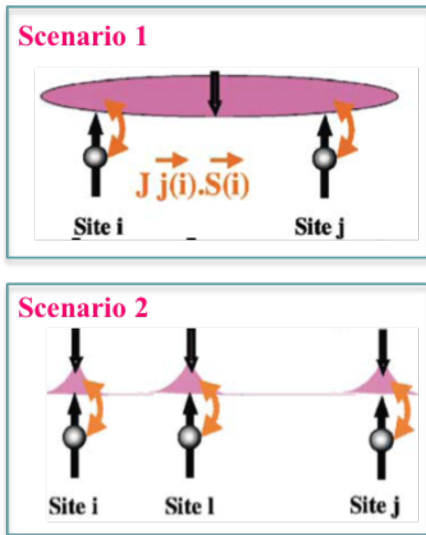


FIG. 8: Schematic of role of carriers in two scenarios for carrier-induced ferromagnetism in dilute magnetic III-V semiconductors.
Scenario 1: Delocalized holes form a Fermi liquid. Coulomb effects are approximated.
Scenario 2: Holes form an almost localized tight-binding band. Fluctuation effects due to randomness and hole-hole correlations are approximated.

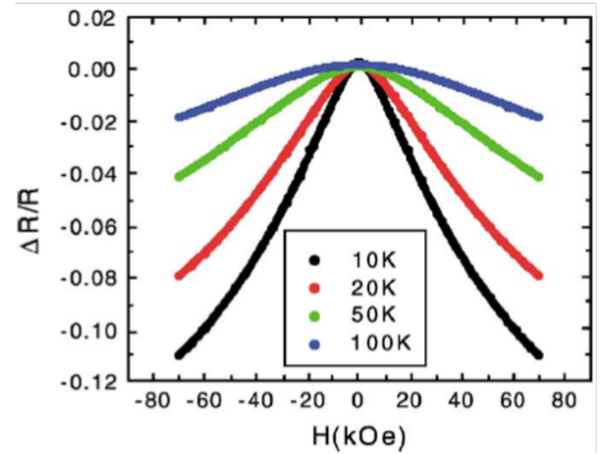


FIG. 9: Magnetotransport data from GaMnN grown at $T_G = 925^{\circ}$C on a GaN buffer[1]

## B. Magnetotransport Properties

### 1. *Negative Magnetoresistance*

When magnetic ions are doped into semiconductor to form DMS, spin from magnetic ions can capture carriers into its ferromagnetic spin cluster, due to spin-spin exchange coupling between carriers and magnetic ions. The above procedure produces so called bounded magnetic polarizer (BMP). However, with increased external field, BMP will be destroyed more and more, thus lead to more and more leased carriers to conduct. Therefore, DMS will display a negative magnetoresistance at low temperature.

H. Ohno studied $Ga_{1-x}Mn_xAs$ DMS. The samples displayed as both metal and insulator depend on Mn dose. He discovered that for metallic samples, negative magnetoresistance will intense with decreased temperature, and reached its highest at Curie temperature $T_c$. While for insulating samples, negative magnetoresistance was still stronger even with temperature lower than $T_c$, and external magnetic field effected strongly on sample's magnetoresistance at low temperatures[6]. Fig. 9 shows clear negative magnetoresistance (11% at 10K) on a GaMnN sheet.

### 2. *Abnormal Hall Effect*

Abnormal Hall effect is observed in DMS materials with external magnetic field, which is another important characteristic fact on DMS magnetization. This effect can be expressed by the following relation:

$$R_{Hall} = \frac{R_0}{d}B + \frac{R_S}{d}M, \quad (1)$$

where $R_0$ is normal Hall Effect factor, $R_S$ is abnormal Hall Effect factor. It is observed that $R_S$ is proportional

to surface Hall resistance $R_{sheet}$, i. e., $R_S = dcR_{sheet}$, where $c$ is a constant independent of temperature.

### 3. Enhanced Magnetophotonic Effect

Enhanced magnetophotonic effect is another unique property of DMS, angle change of polarization plane (Faraday angle) can display magnitude of interactions between d, p and s electrons. Theoretical analysis indicates that, Faraday angle $\theta_F$ can be expressed as:

$$\theta_F \approx \frac{\sqrt{F_0}}{2hc}\frac{\beta-\alpha}{gM_n\mu_B}M\frac{h^2\omega^2}{(E_g^2-h^2\omega^2)^{3/2}}l, \qquad (2)$$

where $F_0$ is a constant, $l$ is sample thickness, $h\omega$ is the energy of incoming photons, $E_g$ is energy gap, $M$ is magnetic intensity of the sample. Here, the value of $\beta-\alpha$ will vary according to different doping percentage of composite atoms.

Experiment implies that Faraday Rotation Effect is much stronger in III-V DMS like (Ga,Mn)As than the original compound GaAs, with a $6\times10^4$deg/cm Faraday Rotation at temperature 10K and magnetic field 0.1T[2].

## V. CONCLUSION AND OUTLOOK

Dilute magnetic semiconductors (DMS) has both semiconducting and ferromagnetic properties, which provides the possibility to manipulate electron charge and spin at the same time, and opens a new field in semiconducting technology to invent new electronic devices. Although research on DMS application is still at the stage of exploration, this field has already present its wide spread future in practice. For example, inserting DMS material into magnetic metal and semiconductor, one can realize ejection of carriers with spin polarization into non-magnetic semiconductor, and this technique can be applied to make spin polarized light-emitting diode[36]. While for certain ferromagnetic/non-ferromagnetic multi-layer structures, like GaMnAs/AlGaAs/GaMnAs[37] etc, by tuning temperature and voltage, one can control carrier concentration in semiconducting layer and magnetic coupling between magnetic layers, this property can be used to produce new magnetic-controled and photonic-controled devices.

The field of DMS is developing in a remarkably fast paste. nowadays researchers mainly focus on fundamental aspect, however with deeper and deeper understanding through theoretical and experimental studies, the collaboration between fundamental and applied research on DMS will be increasingly intense and widespread.

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