Chapter 11

Dilute Magnetic Semiconducting Quantum Dots: Smart Materials for Spintronics

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Additional information is available at the end of the chapter

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Abstract

The present day world involved in the fabrication of miniaturized smart devices is in continuous quest of materials with better optoelectronic and magneto-electronic efficiency. Effective incorporation of dopants into semiconductor lattices have been accepted as a primary means of controlling electrical, optical, magnetic and other physico-chemical properties of semiconductors. Manipulations in magnetic spin within a semiconducting material have lead to an effective research for potential ferromagnets with semiconducting properties, leading to an important field, dilute magnetic semiconductors (DMS). On the other hand, quantum dots (QDs) have been registered to be quantum confined nanocrystals with unique optoelectronic properties, having a wide range of potential applications. QDs experienced rapid development leading to the concept of dilute magnetic semiconducting quantum dots (DMSQDs), where transition metals with a few to several atomic percentages, having unpaired d-electrons, are doped in order to manipulate their opto-magnetic properties. These materials are fabricated by alloying transition metals with Group II-VI, III-V and IV-IV elements resulting in multi-component systems. They have tremendous applications in the spintronics industry, where electronic properties are controlled by spin degree of freedom. The present report reveals the significance, electronic origination of the fact, synthesis and their applications toward the fabrication of spintronics devices.

Keywords: dilute magnetic semiconductors, quantum dots, dilute magnetic semiconductors quantum dots, spintronics, opto-magnetic properties

1. Introduction

The dilute magnetic semiconductor quantum dots (DMSQDs) are basically the combination of semiconducting quantum dots, where transition metals are introduced as impurity or dopants. They are symbolically represented by $A_{1-x}M_xB$ or A(M)B or AB(M), where A is often a

non-magnetic cation, A and B can be from Group II-VI, Group III-V and Group IV-IV elements. These nanoscale materials play an important role in microelectronics and magnetic storage devices [1–3]. Additionally, these materials have the quality to exist in both Curie temperatures (T_c) as well as in room temperature (RT) with high saturation of magnetization (M_s) [4–6]. These quantum confined materials has unique magneto-optical and optically controlled magnetism properties, which make them essentially important in today's research on materials for spintronics (spin-based electronics) [7, 8] device making. The device making includes miniaturization of electronic devices, magnetic fluids and high density data storage systems [9–11]. The semiconducting quantum dots which are being in research are from the Group II-VI and the dopants are transition metals. The individual potentiality of these materials, generated by coupling of diluted magnetic semiconductor (DMS) and quantum dots (QDs), is expected to be a path breaking one in the future field of optoelectronics and magneto-optoelectronic devices. To understand better, we will first look into the concept of DMS and QDs separately.

2. Dilute magnetic semiconductor (DMS)

Magnetic semiconductors are the semiconducting materials, which can exhibit ferromagnetism. Doping of the transition metals in these materials are said to be dilute magnetic semiconductors (DMS). The DMS are therefore semi-magnetic due to the introduction of magnetic elements in their lattices. Basically, the spintronics property of these materials has attracted the present day research for possible technological applications. By definition, spintronics is a combination of electrons' spin and their associated electronic charge and magnetic moment.

The first generation spintronics devices are derived from passive magnetoresistive sensors [12], but the second generations devices are expectedly achieved with the active spin-based devices, which are manipulated in the host semiconductor with spin-polarized electrons [13, 14]. The thought behind a spintronics device is the presence of spin-polarized electrons which travels through the host. Although the introduction of the ferromagnetic material in the semiconductor material through doping is extensively studied, yet the electronic spin is difficult to preserve throughout the material interface due to the difference in electrical conductivity in both the doped as well as the host material [15]. Hence, to present these materials as expected material, better than both ferromagnetic and semiconductor individually, research is very much crucial and warranted in spin electronic carrier device industries. DMS is next concept to meet the vital applicative operation to establish the spintronics carrier devices, an efficient one. In DMS, the host is non-magnetic semiconductor, whereas, the magnetic material is from transition metal series. These are powerful integrated devices having highly spin-polarized capacity.

3. DMS materials and their applications

3.1. $A^{II}_{1-x}Mn_xB^{VI}$ ternary materials

One of the most extensively studied DMS is alloys of $A^{II}_{1-x}Mn_xB^{VI}$ (*A- Group II element & B-Group VI element*) [16]. This ternary material exhibits both wurtzite and zinc blende crystalline

structure as per their compositional range [17]. It is noticed that the change in Manganese (Mn) content can lead the crystal structure to cubic or hexagonal orientation. It has been observed that lower the input of Mn element in the host composition, the resultant structure tends to acquire cubic crystallinity, whereas, with higher the amount of Mn doping wurtzite crystallinity is observed [18]. Crystal structure of the various compositional ranges of the material suggests that, although their symmetry is different, both achieve tetrahedral geometry (s-p^3 bonding) with the involvement of 2*s* valence electrons from Group II element and 6*p* valence electrons from Group VI element. Mn acts as a contributor of its valence $4s^2$ electrons to the s-p^3 bonding arrangement, although Mn differs from Group II material with an exactly half-filled d-orbital. The Hund's rule suggests that introduction of an unpaired electron of opposite spin will require a lot of input of energy (~ 6–7 eV) and hence Mn is acting as complete *3d* shell material [19]. This ability makes Mn eligible for the replacement of Group II elements in the tetrahedral structure. There is another crucial reason behind the establishment of Mn as a replacement of other Group II materials, which is the exact half-filled *3d* orbital configuration of Mn. The fact is as important as, there is a possibility of forming stable phase by other elements too, although, dimer formation is very much a possibility for other than Mn of the Group II element [18].

3.2. TiO_2 base DMS

Among the oxide base DMS materials, Cobalt (Co) intruded Titanium dioxide (TiO_2) system is one of the most consistently researched *n-type* semiconductor, to achieve ferromagnetism far above the RT ($T_c > 650$ K) [20]. The importance of temperature in this kind of system is because the system of magnetic semiconductor is hard to achieve at RT [21, 22]. The reason behind such concept is the faced difficulty in the introduction of both electronic and magnetic dopants in the system and functionalization of the designed material as a good balanced material between dopant spins and free carriers of electrons. Hence, the synthesized material achieves the coupling as a thermally strong dopant spin-carrier coupling [22]. The most recent research suggest that the ternary cited materials of Mn-doped Group II-VI semiconductors are also capable of exhibiting the expected necessary property as Co-doped TiO_2 revealed at RT [23, 24].

TiO_2 is a wide direct forbidden band gap (3.03 eV) material, used for optoelectronic devices and solar cell applications [25–27]. Its crystal symmetry is found to be in tetragonal and rhombohedral orientations [28]. Therefore the thin films of Co-doped TiO_2 can be accommodated in the applicative DMS devices. The first observation of RT ferromagnetism in the Co-doped TiO_2 system was reported at Anatase phase $Ti_{1-x}Co_xO_2$ films ($0 \le x \le 0.08$), on $LaAlO_3$ and $SrTiO_3$ substrates, using laser molecular beam epitaxy, at substrate growth temperatures between 680 and 720°C [29]. Same research group also found the satisfactory results with the thin films of rutile phase TiO_2 with a composition of $Ti_{1-x}Co_xO_2$ ($0 \le x \le 0.05$) onto α-Al_2O_3 substrates, using the same deposition technique [30]. After this achievement, a good number work on this composition was done with various thin film deposition techniques, viz., pulsed laser deposition (PLD) [31–36], laser molecular beam epitaxy (LMBE) [37–39], metal–organic chemical vapor deposition (MOCVD) [40], reactive co-sputtering, oxygen-plasma-assisted molecular beam epitaxy (OPA-MBE) [41] and sol–gel [42] method. Researchers observed that the pressure of Oxygen applied during the thin film deposition is also a very important factor and suggested that at $P_{O2} \ge 1.3 \times 10^{-5}$ mbar, we can have clear streaky RHEED patterns, which suggest two-dimensional smooth surfaces [32].

The ferromagnetism in Co-doped TiO_2 is a topic of interest for the research accompanying spintronics devices. The oxide base DMS materials have extrinsic or intrinsic effect, which is the root of their device driven capability, is still a matter of discussion. The extrinsic effect may be attributed to the interaction of local magnetic moments with magnetic impurities. The intrinsic magnetism may be due to the exchange coupling between the spin of carriers and local magnetic moments. Since, spintronics takes place only in polarized charge carriers, which is possible only when the ferromagnetism is intrinsic. The issue is of great concern because the experimental evidence is not yet available behind the actual reason of magnetism of DMS in TiO_2. Anomalous Hall effect (AHE) and electric field induced modulation by magnetization suggests, for rutile phased Co-doped TiO_2 system, the carrier-mediated ferromagnetism with a value of 13.5% [43, 44].

Recent theoretical studies propose the creation and distribution of oxygen vacancies in Co-doped TiO_2 is responsible for the ferromagnetism in these systems. The ferromagnetism is suppressed when the oxygen content is increased in the unit cell [45]. In a nutshell, for the TiO_2 crystal, in the event of an oxygen vacancy, Ti atoms will give away their electrons to oxygen and hence they will be in the scarcity of electrons to get bind with the oxygen vacancy sites by their own atoms and therefore a situation of hydrogen-like orbital occurs, hence constitutes a Polaron. This phenomenon is supported by a percolation model named bond magnetic polaron (BMP), which was used to study the magnetically doped oxides [46].

In the interaction of the magnetic cations with the hydrogenic electrons in the impurity band, the donors tend to form BMPs, coupling the 3d moments of the ions within their orbits. Depending on whether the cation 3d orbital is less than half filled, or half filled or more, the coupling between the cation and the donor electron is ferromagnetic or anti-ferromagnetic, respectively. Either way, the coupling between two similar impurities within the same donor orbital is ferromagnetic. The polaron radius is a function of the host material's dielectric constant and electron effective mass. If the polaron concentration in the material is large enough to achieve percolation, an entire network of polarons and magnetic cations become interconnected and we observe macroscopic ferromagnetic behavior [47].

Thus, the incorporation of impurities/dopants in the semiconducting lattices have been realized as an important primary means of controlling the magnetic and electrical conductivities, besides having an immense effect on magnetic, magneto-optical and other physical properties of semiconductors.

4. Quantum dots

Quantum dots (QDs) of semiconducting materials have attracted the research community due to their potential application in various fields of humanity, viz., optoelectronics, solar cell, bioimaging and biosensors, cosmetics, space science, photocatalytic activity, etc. [48–54]. The QDs can be defined with respect to their size, which is supposed to be less than excitons Bohr radius. The material specific Bohr radius also leads to the property of that material. The size factor is supported by differently shaped particles. The size of the QDs leads to the significant change in band gap of the semiconductors than the bulk. The enhanced band energy of the particles is

due to the fact of their atom like structures. These particles in this confinement have 10–1000 numbers of atoms within one particle. Therefore, the energy levels of each particle have the merging levels of only some of the atoms in comparison to their bulk entity, where millions of atoms coincide. Because of this fact, very less energy levels can merge with each other in a QD and hence the band gap energy increases drastically. The QDs have another specific property of showing blunt and broad absorption peak. The primary cause behind the phenomenon resides in their size effect. At the atomic level, the slight change in the size of a particle (viz., 0.5 nm) can change their HOMO-LUMO gap drastically. Therefore, whenever there is a solution of QDs, the particle size is never homogeneously uniform in the solution. Hence, for every particle the band gap energy will be different and therefore the absorption maximum shifts accordingly. As a consequence of the presence of differently sized particles in the solution, togetherness of these absorption maxima can be observed and hence a broad peak. Therefore, by tuning the size, we can meet the desired application with these particles. Apart from the size factor, shape phenomenon also plays a significant role in deciding the characteristic features in the field of quantum dot physics. The electrons, which are the driving force behind every electronic transition in a physical matter, have received different orientations in terms of surface of the particle. In the quantum range of physics, the QDs are forced to adapt the required application by modifying their surface. The reason behind such observation is the attachment of the surface electrons for differently shaped particles is different, which is again as an outcome of releasing surface energy of the particle to make it stable. The introduction of capping agents (the ligands) is also having a capability of taming the particle according to their preferred shape. This phenomenon is addressed as surface functionalization. The surface modification can lead us to the fabrication of the particles with better efficacy in different applicative devices.

The property of showing high luminescence by these QD metamaterials is one of the most aspired properties. The generation of double excitons leads the materials toward more promising luminescent material. This extraordinary property blesses these materials to show higher emission range than the traditional dyes and hence they become more appropriate with the fact of getting more emission with the excitation of only one electron. The size and, of course the shape, both have an important role in making them suitable for these applications. Most of the time the tunable size property of these quantum dots is mentioned, due to which one can access the whole light spectrum. The devices such as LEDs and solar cell require these nano dots in such a manner that they have the ability to absorb the whole visible and UV region and emit the same in higher wavelength. Therefore, the luminescence property of these fluorescent dots has to have the tenability to perform in the whole region. Fortunately, researchers found that for different semiconducting quantum dots, we can achieve the luminescence as per our requirement. Another interesting concept of wastage of the solar energy as thermal energy during the absorption of sun light by a photovoltaic cell comes into play, in the present day photo voltaic research. It is observed that a photovoltaic material, such as, QDs (although being the most promising one), cannot absorb the whole sun light as conversion efficiency of the cell becomes less. The reason behind this is the material, that we are using, can absorb the light in the desired range but cannot emit the same in the desired wavelength. To tackle this difficulty, the concept of large stock shift quantum dots has come up. This large stock shift materials can absorb the sun light in short wavelength and emit the same in the long wavelength, which make these functionalized quantum dots more efficient toward these kind of applications [55].

5. Dilute magnetic semiconductor quantum dots (DMSQDs)

Discussions on DMS and QDs have made it easier to understand the concept of DMSQDs. They are quantum dots of semiconducting materials doped with transition metals having magnetic behavior. Due to specific significance of QDs, researchers are tremendously focusing on the ferromagnetic material doped QDs. Since, semiconductors do not possess high magnetism in any level of their atomic growth, it becomes essential to incorporate the magnetic nature of DMS in nanoscale so as to improve its efficiency in the various fields of spintronics applications. It has been observed that the effectiveness of interaction of *sp-d* for the exchange of carrier and magnetic ions in terms of hole energy depends on the high and low magnetic field induces from outside. Hence, it is expected that due to the small size of a quantum dot, the exchange and interaction of *d* electrons with *sp* shelled electrons will be extensive in DMSQDs [56]. Therefore, the spintronics devices developed from DMSQDs are expected to be efficient as well as miniaturized one, probably due to the quantum confinement effect of DMS and therefore better than the single DMS materials.

5.1. Synthesis of DMSQDs

The synthesis procedures are very much similar to those for the synthesis of QDs. The only exception is to incorporate the metallic materials as impurity during the reaction process. Among a vast number of procedures, the chemical route to synthesis DMSQDs is the most commonly use deficient method. The size and shape of such QDs can be easily tailored through this method. Unwanted oxidation can also be prevented during the adopted during the synthesis process. Fe, Co, Ni and Mn are the main doping elements used for the preparation of DMSQDs of semiconductors of Group II-VI [56].

Clustering and surface doping are two main issues that are faced during the synthetic process for obtaining uniformed DMSQDs. To eliminate these key issues, one has to overcome self-purification [57] of the materials and understand the reactivity between the host-guest materials [58, 59]. The self-purification is a process where host molecule expels the guest molecule from the surface to attain a thermodynamically stable state by reducing its defect energy. Self-purification can be resolved by making the magnetic core at first, followed by coating with the semiconducting material and then annealing at higher temperature for a longer time to diffuse the dopant inside the host properly before it get expelled by the host. The reactivity issue can be sorted out by two ways: a) Nucleation doping and b) Growth doping. Successive ionic layer adsorption reaction (SILAR) method was used to dope Fe in CdS in one of the methods of its preparation. This was attained at high temperature. This method showed excellent result with the homogeneous diffusion of Fe in CdS shell. It was also reported that the oxidation state of Fe was reduced to 2 from 2.44 due to the presence of reducing reagent and replaced the Cd site with substitutional doping.

5.2. Properties and applications of DMSQDs

DMSQDs possess unique properties which make them suitable for wide range of applications. Their properties are primarily divided into magnetic and magneto-optical as well as magneto-electrical properties. These properties are attributed to the exchanged interaction

of *sp-d* between the dopants magnetic material and the host semiconductor, although proper mechanism of origin of the effect and the governance of ferromagnetism are not yet confirmed. Secondly, it has been observed that due to the presence of quantitatively unknown weights of ligands within the synthesized material makes it difficult to calculate the conversion of magnetic moments from magnetic ions, [60] however there have been improvement toward the production of DMSQDs from time to time. Early reports on quantification showed the presence of a few magnetic moments in emu/gram (memu/g) [61] due to the doping of magnetic ions, instead of much more as expected. The effect of unknown amount of magnetic moment hinders the knowledge of comparison between the absolute magnetism of bulk and nano materials. The plausible reason to this effect may be the clustering of magnetic dopants or/and inherent *sp-d* exchange interactions.

One of the most advantageous finding on DMSQDs shows an exceptionally different nature of magnetism. It is the co-doping of ZnO with Cu and Fe [62]. Interestingly, ZnO individually doped with Fe or Cu showed an anti-ferromagnetic behavior without a trace of ferromagnetism. Whereas, the co-doping of both the transition metals in ZnO showed high quality ferromagnetism with magnetic moment as high as 600 memu/g. This work has proved the anti-ferromagnetism of Cu doped ZnO with the help of *M* versus *H* (Magnetization versus Magnetic field intensity) plot and anti-ferromagnetism of Fe doped ZnO with the inverse susceptibility plot as function of temperature, showing a negative intercept. But, in co-doped ZnO with Cu and Fe, X-ray absorption spectroscopy (XAS) clearly showed the presence of both Fe^{+2} and Fe^{+3} and its relative percentage is dependent on the presence of Cu as a dopant. Another research revealed that the size of Fe doped CdS QD was responsible for the magnetic moment [57]. They have achieved a magnetic moment of 80 memu/g at RT for doped CdS and undoped CdS showed negligible amount of magnetic moment with the same scale reaction. It has been observed that in the presence of an external magnetic field, a non-magnetic substance showed a small internal magnetic field due to Zeeman splitting (having an order of 2), whereas, materials like DMSQDs, the intensity of internal field is very high in the presence of external magnetic field [56]. It is also observed that along with the large internal field, a small external magnetic field also gets generated during this process. This happens due to the presence of the magnetic ions inside the material and the tendency to align themselves in the direction of the applied magnetic field. Theoretical modeling of magneto-optical and electronic property of core-shell nanoparticles of CdS-ZnS, doped with magnetic impurities of Mn showed that, these nanocrystals can give an attuned value of *g* over a wide range and make them suitable for spintronics devices, if the position of the magnetic impurities can be controlled [63]. Spectral fingerprints of the spin–spin interactions between the host excitons and the dopant is also revealed by single particle spectroscopy with discrete projections of individual Mn^{+2} ions observed from emission peaks. These QDs showed enhancement in exchange splitting at elevated temperatures by an order of magnitude compared to their epitaxial counterparts, which is useful for solotronics applications. The circularly polarized photoluminescence in the presence of magnetic field (MCPL) for bulk DMS is very much different than the QDs. In case of DMS material, the emission band edge of the host material showed a polarization due to the splitting of the band, but doped material (Mn^{+2}) do not show any band polarization due to spin and orbital forbidden emission [64]. But, in DMSQDs, along with the host, the dopant also showed polarized emission band edge in the presence of magnetic field. This surprised effect was although not yet properly understood, but expected to be due to quantum confinement,

where wave functions are overlapped extensively [65]. Magneto-optical response in Cu doped chalcogenide QDs is also a tremendous effect observed in DMSQDs. This photo-excitation phenomenon in these DMSQDs has come as a result of strong spin-exchanged interaction between the valence band-conduction band (VB-CB) of the host and the paramagnetic Cu dopant. The magnetic circular dichroism (MCD) studies revealed the enhancement of paramagnetism up to 100% in these Cu doped ZnSe/CdSe QDs under the UV light excitation. Again, in dark, these materials retained a photo-magnetization memory for timescales of hours [66]. Another application is reported for Mn-doped CdSe QDs as light-induced spontaneous magnetization, where spin effect is controlled to generate, manipulate and read out spins [67]. In this case, no external magnetic field was applied but still showed large Zeeman splitting as a result of photo-excitation. The reason behind these giant splitting is the generation of large dopant-carriers exchange fields. These materials are having potential applications in the field of magneto-optical storage and optically controlled magnetism. DMSQDs are also known to respond to charged carriers. The carrier-mediated ferromagnetic interaction in Mn-doped CdSe QDs are also reported, which arise due to photo-excited carriers from surface defect states of smaller QDs (~3 nm) [68]. Mn-doped ZnO QDs also exhibited ferromagnetic exchange interaction due to photo-excitation in the absence of oxygen [69] and as is reported in air-stable Fe–Sn co-doped In_2O_3 [70]and Mn–Sn co-doped In_2O_3 [71]. Research has proved the conduction band electron–dopant ferromagnetic exchange interaction, offers magneto-electric and magneto-plasmonic properties which helps in wide scale spintronics applications.

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