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Role of Hydrogen in Variation of Electrical, Optical and Magnetic Properties of ZnSe-Fe Bilayer Thin Films Structure

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Abstract

This paper is reporting the role of hydrogen in preparation and characterization of dilute magnetic semiconductor of ZnSe-Fe bilayer thin film structure. These films are hydrogenated at different pressure to see the effect of hydrogen on electrical, optical, magnetic and structural properties of bilayer structure. Optical absorption in thin films is found to be decrease with hydrogen absorption. It may be due to interaction of hydrogen with bilayer structure and takes electron from the conduction band of thin film structure. The current-voltage characteristic of these films shows the variation in conductivity with hydrogenation due to decrease in electron density. Atomic Force Microscopy and scanning electron Microscope recorded to see the surface topography of bilayer thin films. It has been observed that deposited film have nano size structure that is favorable for hydrogen absorption having higher surface to volume ratio. The Electron diffraction X-ray analysis gives the information about composition of films. Raman spectra have used to see the presence of hydrogen. Super-conducting Quantum Interference Device gives the information of confirmation of diluted magnetic semiconductors and variation of magnetic momentum with hydrogenation.

Key words: Thin film; Atomic Force Microscopy; X-ray diffraction; Scanning electron microscope (SEM); Electron diffraction X-ray analysis (EDAX); Hydrogenation

INTRODUCTION

Modern information technology utilizes the charge degree of freedom of electrons to process information in semiconductor and spin degree of freedom for mass storage of information in magnetic materials. If both charge and spin degrees of freedom are available in semiconductors then we are able to create new functionalities and enhance the performance of existing devices. To do so, we required to create sustain, transport, control of spin and also detect spins in semiconductors, which is a challenge for semiconductor physics, materials and science technology.

In recent years there is a tremendous research interest in the introduction of ferromagnetic property at room temperature in semiconductors to realize a new class of spintronic devices such as spin valve transistors, spin light emitting diodes, non-volatile memory, logic devices, optical isolators and ultra-fast optical switches (Chambers, 2002). Diluted magnetic semiconductors (DMS) have been studied actively for the use of both charge and spin of electrons in semiconductors. Spin injection into non-magnetic semiconductors was trying by many research groups to offer a new classes of spintronic devices. Diluted magnetic semiconductors, in which transition metals are doped into semiconductors exhibiting room temperature ferromagnetism, have also attracted much attention for their potential uses in spintronic devices (Pan, Song, Liu, Yang, & Zeng, 2008). The use of carrier spins, in addition to carrier charges, of spintronic devices looks promising research field of magnetic recording media (Pearton, et al., 2003). The advantages of diluted magnetic semiconductor (DMS) based spin-electronic devices include enabling of instant-on computer, increased integration density, higher data processing speed, low electrical energy demand and compatibility of their fabrication processes with those currently used in industry.

Banerjee and Ghosh (2008) fabricated $Cd_{1-x}Mn_xTe$ thin films using thermal inter-diffusion of multilayers of sputtered compound semiconductors. They had observed that addition of Mn-content in CdTe has resulted increase band gap and also activation energy but found decrease in resistance under illumination. Single crystal of $Zn_{1-x}Mn_xTe$ was prepared successfully by vertical Bridgman technique for different concentration of Mn and it was also found that band gap increases with increasing concentration of Mn (Brahmam, Reddy, & Reddy, 2005). Daboo et al studied the switching behavior of Fe/GaAs samples for various values of uniaxial and cubic anisotropy constants using in-plane MOKE magnetometer (Daboo, et al., 1994). Growth of Fe-films on ZnSe epilayers and bulk GaAs substrates investigated by Bierleutgeb Sitter, Krenn, and Seyringer, (2000) to determine the mode of film growth as well as structural properties of the films. The effect of varying Fe and ZnSe semiconductor layers thickness on the magnetic and electronic properties of the super lattice analyzed by Continenza, Massidda, and Freeman (1990). They had found that Fe magnetism recovers its bulk characteristics and the enhanced magnetic moment was quickly suppressed as the number of layer increased. Meckenstock, et al. (2002) investigated the Magnetic properties of Fe/ZnSe and Fe/GaAs hetero-structures by ferromagnetic resonance and SQUID measurements and found that (001) Fe-films on GaAs and ZnSe substrates show steps in the hysteresis. Kerbs, Jonker, and Prinz (1987) reported the magnetic properties of single-crystal α-Fe films grown by molecular beam epitaxy (MBE) on both (110) and (001) ZnSe epilayers. The origin of the uniaxial in-plane anisotropy found in (110) Fe/ZnSe and (110) Fe/GaAs films is attributed to the combination of magneto restriction and the lattice mismatch-induced strain originating at the Fe/substrate interface. It was found that Fe/ZnSe films have more attractive properties to compare Fe/GaAs.

Hydrogen is an important impurity in many semiconductors because of its tendency to form complexes with most crystal defects and impurities. In combination with its presence during crystal growth and processing, hydrogen has gained both fundamental and technological interest (Pankove, & Johnson, 1991; Pearton, Corbett, & Stavola, 1992; Pearton, 1994; Estreicher, 1995; Pavesi & Giannozzi, 1992) because hydrogen strongly affects the electronic properties of materials. Extensive experimental and theoretical work on hydrogen in silicon has led to a more detailed understanding of its properties in this material compared to all other semiconductors. Interstitial hydrogen is a fast diffuser. It can bind with native defect or other impurities, often eliminating their electrical activity-a phenomenon known as passivation. Electrical measurements such as current/voltage provide detailed information about the electronic effects of hydrogen. Nehara et al (2009) observed the effect of hydrogen on electrical properties of CdTe/Mn bilayer thin films and suggested variation in electrical properties with hydrogenation. Thevenard et al (2007) prepared perpendicularly magnetized (Ga,Mn) As layers using a monoatomic hydrogen plasma and suggested that original magnetization reversal phenomena arise from the presence of a soft magnetic interface between the ferromagnetic and paramagnetic regions, and that undergoing hydrogenation indeed leads to their efficient passivation. The reduction of Hole density resulted in strong modifications of their ferromagnetic properties. In particular, Thevenard, Largeau, Mauguin, Lemaitre, and Theys (2005) observed in magneto-transport experiments that the decrease of the Curie temperature, along with modifications of the magnetic anisotropy, a behavior consistent with the mean-field theory. Hydrogen can also induce electrically active defects, adsorption of hydrogen on the TiFe (110) surface covered by palladium monolayer was investigated by Kulkova, Eremeev, Egorushkin, Kim, and Oh (2003) using the full potential linearized augmented plane wave method within the local density approximation. An author Park et al. (2007) observed that the interstitial hydrogen leads to the changes in the magnetic hysteresis loop as well as the enhancement of carrier concentrations in the Mn-doped ZnO film. Hydrogen molecules at normal pressure are infrared inactive due to their lack of dipole moment, but studied by Raman scattering (Stoicheff, 1957) gives information that hydrogen strongly affects the optical properties of diluted magnetic semiconductors. It was also observed that optical transmission spectra found to decrease and optical band gap found to increase due to the hydrogenation in CdTe-Mn bilayer DMS thin films (Nehra & Singh, 2009). The Raman spectroscopy carried out by many authors to get information about the presence of hydrogen in semi conducting materials (Vetterhoffer, Wagner, & Weber, 1996; Pritchard, Ashwin, Tucker, Newman, & Lightowlers, 1996; Leitch, Alex, & Weber, 1998).

The incorporation of magnetic ions with semi conducting materials is an increasing active area of research. Since interfacial effects are expected to play an important role in thin film hetero-structures of DMS resulting in a broad range of magnetic properties depending on the film thickness and deposition conditions. We are presenting preparation and characterization of hydrogenated ZnSe/Fe bilayer DMS thin films grown ZnSe by thermal evaporation technique and Fe by D.C sputtered. These films are characterized by various techniques as XRD, AFM, and UV-Vis spectrophotometer, scanning electron microscope (SEM), EDAX for elemental analysis and SQUID used to determine magnetic properties, Raman spectroscopy for confirm the presence of hydrogen.

1. EXPERIMENTAL DETAILS

1.1 Method of Preparation of Bilayer Thin Films

ZnSe/Fe bilayer thin films were deposited on glass substrates in a vacuum better than 10^{-5} torr by using thermal and sputtered method respectively. Compound zinc selenide powder (99.99 % purity) procured from Alfa Aesar, Jonson Matthay Company, U.S.A. First we have deposited Fe layer and later ZnSe, to obtain ZnSe/Fe bilayer thin film structure. The thickness of ZnSe/Fe bilayer DMS thin films was 250 nm (100 nm Fe/150 nm ZnSe) measured by quartz crystal thickness monitor and then such a bilayer of ZnSe/Fe thin films have been annealed in vacuum at constant temperature of 500^0C for one hour at base pressure 10^{-5} torr . Anneling process was helpful to get homogeneous structure and inter diffusion of bilayer thin films. Hydrogenation of ZnSe/Fe bilayer thin films have been performed by keeping these samples in hydrogenation chamber, where hydrogen gas was introduced at different pressures for 30 minutes.

1.2 Characterization Techniques for ZnSe/Fe Thin Films

The X-ray diffraction (XRD) patterns of as grown and vacuum annealed DMS thin films is recorded with the help of PANalytical X'pert PRO MPD PW3040/60 X-ray diffractometer using CuK_a radiation. The SEM and EDAX analysis carried out by using special addition ZESIS EUO-18 model at USIC, University of Rajasthan, Jaipur to see the surface morphology and elemental composition of film... The XRD patterns of films are recorded in the range from 20° to 80° (2 theta) to see the structure of as deposited and annealed films. Transverse I-V characteristics of as grown films and annealed films with hydrogenation have been recorded using Keithley-238 high current source measuring unit. The I-V characteristics of bilayer thin films have been monitored with the help of SMUSweep computer software. The atomic force microscopy (AFM) 3D images of annealed and hydrogenated thin films were recorded in contact mode to examine the surface topography of composite films using CP-II (Vecco Instruments) at our deparment

M-T and M-H measurements were recorded for these films by Quantum Design superconducting quantum interference device (SQUID) at TIFR, Mumbai (India) to see the effect of hydrogen on magnetic moment. The transmission spectra of as deposited and annealed hydrogenated thin films were carried out with the help of Hitachi Spectrophotometer Model-330 and the Raman spectra of as grown and annealed hydrogenated samples were recorded using Green laser beam of wavelength 532 nm (Raman model-3000 system).

2. RESULTS AND DISCUSSIONS

2.1 XRD Analysis

Structural characteristic of ZnSe/Fe bilayer thin films structure is carried out by XRD as shown in Figure 1. In the XRD pattern there is not appears any dominated peak in as deposited bilayer structure. It may be due to amorphous nature of as-grown bilayer thin film. However the vacuum annealed thin film structure at 333 K shows crystalline nature. This may be due to grain size growth in bilayer structure by annealing. There are few broad peaks observed at 27.40˚, 31.90˚, 54.38˚ and 64.60˚ corresponding to (111), (200), (311) and (200) planes of cubic ZnSe and Fe respectively. There are only two sharp peaks at 44.98˚ and 44.36˚ observed corresponding to (220) and (110) oriented planes of cubic ZnSe and Fe respectively. In case of ZnSe similar sharp peaks were observed by Kalita, Sarma, and Das (2000).

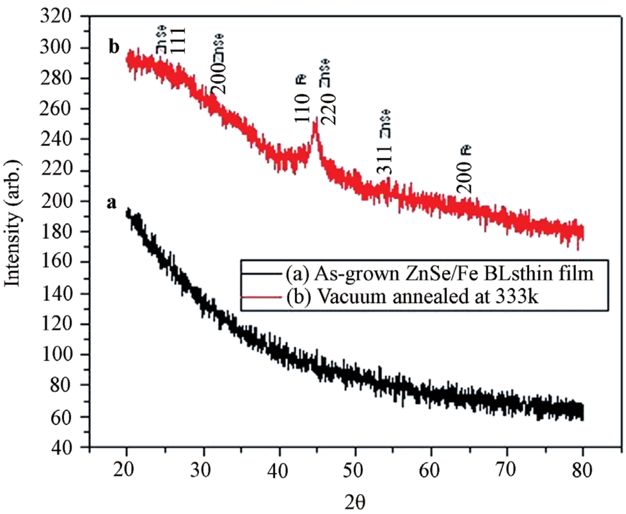


Figure 1
XRD Patterns for (a) As-Grown and (b) Vacuum Annealed ZnSe/Fe Bilayer Thin Films

2.2 EDAX Analysis of Thin Films

Figure 2 (a) shows the EDAX analysis of glass substrate coated with tin oxide. Energy dispersive X-ray (EDAX) revealed that the nano-structure in thin bilayer structure is exist with Sn and Oxygen .The atomic ratio of Sn: O in the film is 83.4 and 16.96 without impurity. Figure 2 (b) also shows recorded spectra of the EDAX analysis for glass substrate coated with tin oxide and deposited ZnSe over it. The all the peaks of Zn, Se and tin oxide appears in spectrum analysis.

Figure 2(c) shows the EDAX analysis of glass substrate coated with tin oxide and Fe/ ZnSe bilayer thin film deposited over it. Energy dispersive x-ray (EDAX) revealed that the nano structure contains predominately Fe, Zn, and Se atoms. The atomic ratio of Fe: Zn: Se is in this film structure is observed as 3.23:43.10:48.54 with small impurity of Ni and Ti. This analysis revealed the elemental analysis of deposited thin film has presence of magnetic ions in semiconductors. That is essential for dilute magnetic semiconductors.

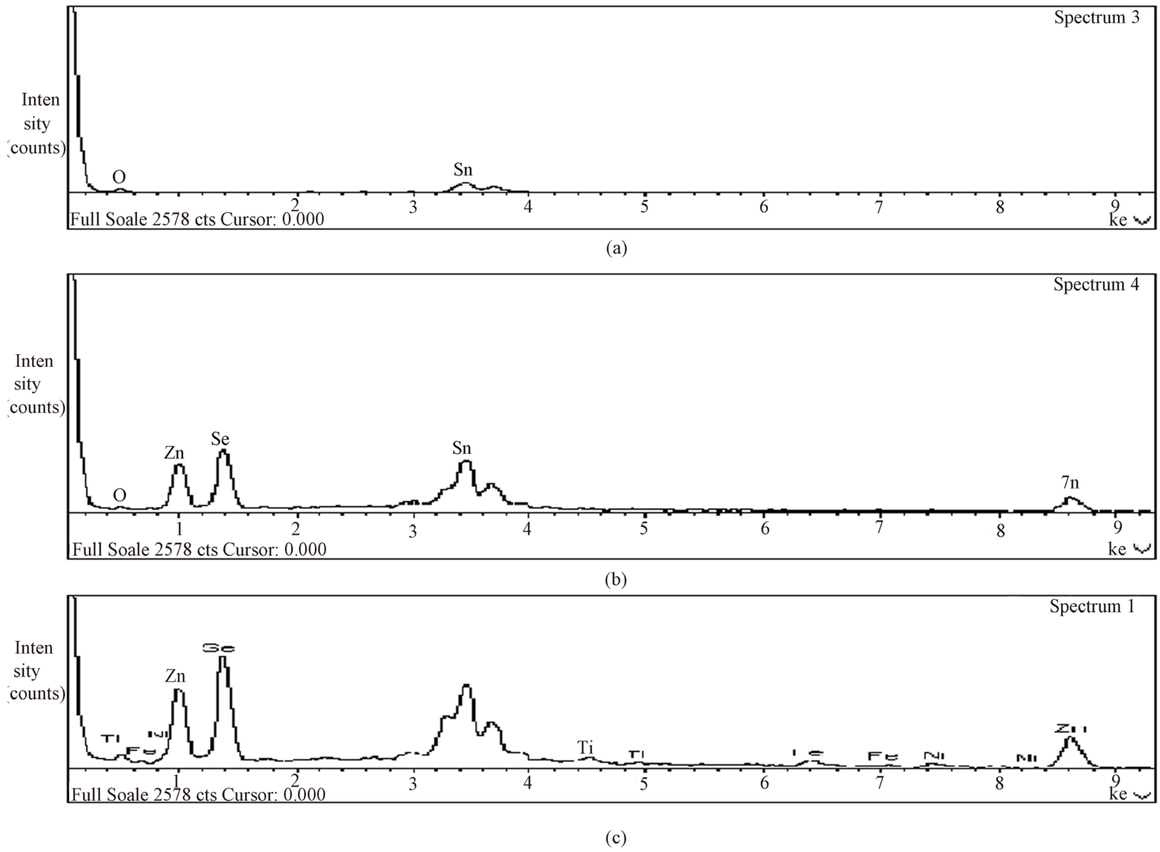


Figure 2
EDAX Analysis (a) Glass Substrate Coated With Tin Oxide (b) ZnSe Thin Film (c) Fe/Znse Thin Film

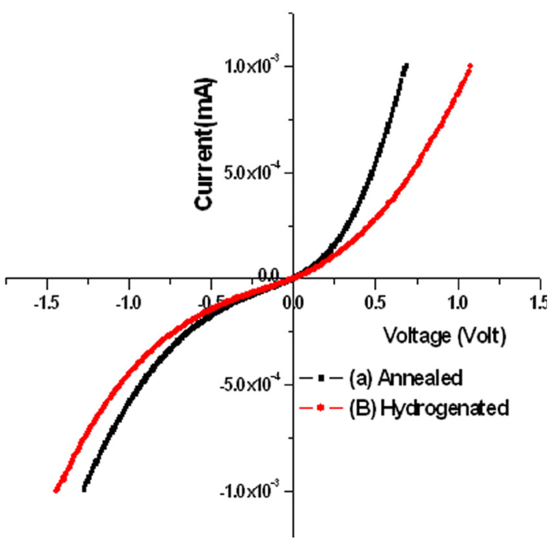


Figure 3
I-V Characteristics of (a) Annealed and (b) Hydrogenated ZnSe/Fe Bilayer Thin Films

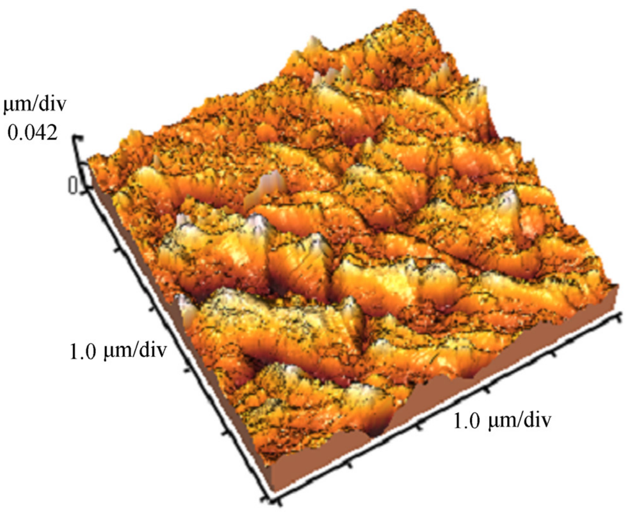
2.3 I-V Characteristics

Figure 3 shows I-V characteristic of annealed and hydrogenated films. This plot shows that the current is found to decrease by hydrogenation compare to annealed film structure. It means hydrogen passivated defects at interface or it takes electrons from Fe and blocks the flow of charge carriers across the interface, hence current decreases in forward as well as reverse direction after hydrogenation. It reveals that conductivity decrease due to hydrogenation. Hydrogen interacts with metals and semiconductors and takes electron from conduction band of metal as interaction of an anionic model. Similar results were observed on CdTe-Mn bilayer thin films by Nehra et al (2009).

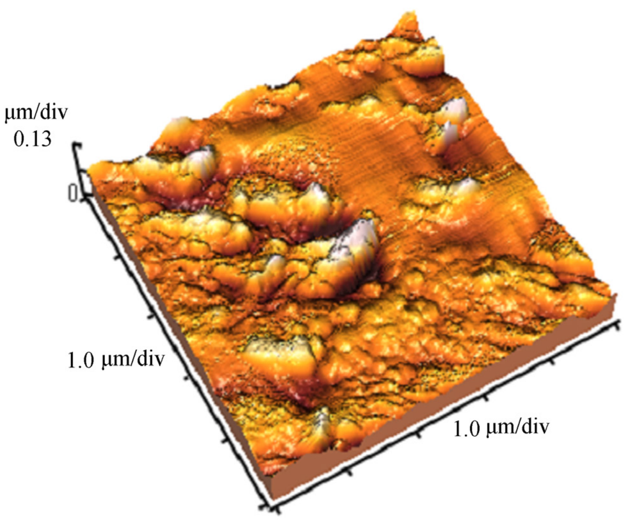
2.4 Atomic Force Microscopy 3D Images

The atomic force microscopy (AFM) 3D images of annealed and hydrogenated thin films were recorded in contact mode to examine the surface topography of composite films using CP-II (Vecco Instruments) at our departmental facility.

The AFM images shown in Figure 4 (a&b) indicate a clear picture of the surface in nanoscale dimensions (5 × 5 μm scan area), where the topography predicts compact grain structure. It is evident that the surfaces of ZnSe/Fe bilayer DMS films are composed with dense grains of elements. The value of surface roughness is found to be 10.12 for annealed sample and increase 20.17 nm with increasing hydrogen pressure. The surface roughness values and peak-to-valley ratio for annealed and hydrogenated ZnSe/Fe bilayer DMS thin films are shown in Table 1. Similar results are also observed by Hao, Zhu, Ong, and Tan, (2006) in the case of hydrogenated Al-doped ZnO semiconductor thin films.



（a）



（b）

Figure 4
AFM Topography 3D Images of (a) Annealed and (b) Hydrogenated ZnSe/Fe Bilayer Thin Films

Table 1
Atomic Force Microscopic Measurements

S.No.	Name of samples (nm)	RMS (nm)	Average RMS (nm)	Peak-to-velly ratio
1	Annealed	10.12	7.75	83.08
2	Hydrogenated	20.17	14.49	253.6

2.5 Scanning Electron Microscope Images

The SEM images of Fe and ZnSe shown in Figure 5&6 with different magnifications clearly indicates the formation of nano structure and nanoclusters. The average grain size length for Fe is around 125-750 nm and Fe/ ZnSe around 70 to 100nm. The EDAX plots of Fe/ZnSe mentioned already in Figure 2(c) with elemental composition. This nanostructure of bilayer is helpful for hydrogen adsorption at surface and interface. Due to hydrogen adsorption electrical, optical and magnetic properties are tailored and reported in this paper with evidence. As observed properties of dilute magnetic semiconductor are of great advantage in future spintronic applications in science and technology

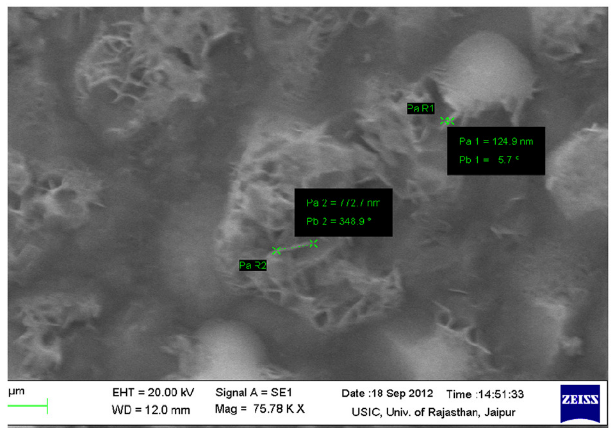


Figure 5
Scanning Electron Microscope Image of Fe Thin Film

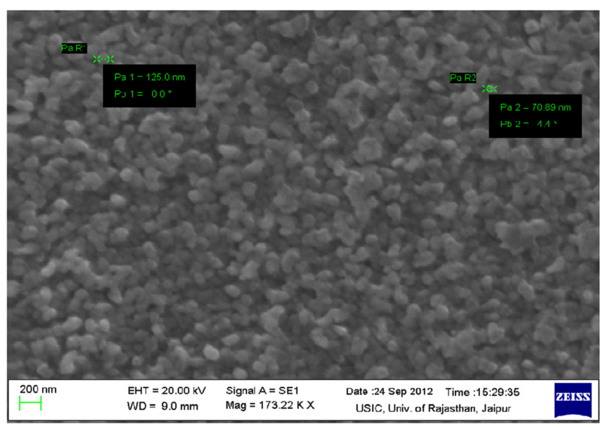


Figure 6
Scanning Electron Microscope Image of Fe/ZnSe Thin Film

2.6 UV-Vis Measurements

Figure 7 shows absorption versus wavelength for as-grown, annealed and hydrogenated ZnSe/Fe bilayer thin films. The absorption spectra of as-grown thin film show decrease in absorption compare to annealed bilayer thin films structure indicating that the mixing of bilayer due to removal of defects by annealing. Hydrogenated bilayer thin films shows higher absorption than as-grown thin film and annealed. It was also noted that absorption is found to increase with increasing pressure of hydrogen. These variations in the absorption spectra are due to the defect passivation by hydrogen adsorption at surface and interface.

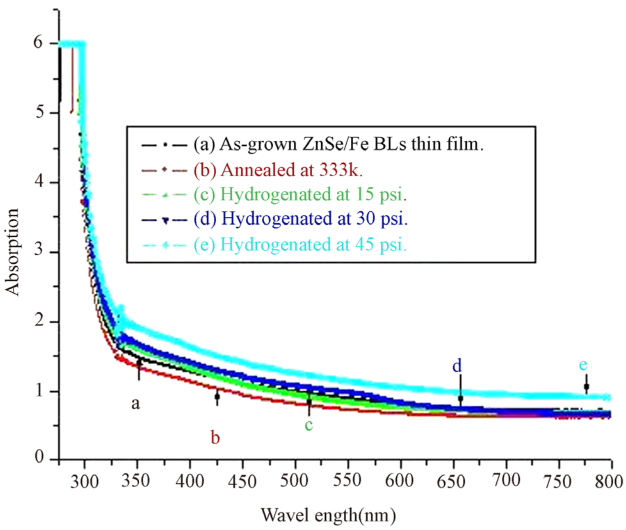


Figure 7
Wavelength Versus Absorption Plots for ZnSe/Fe Bilayer Thin Films at Different Hydrogen Pressure

2.7 Magnetic Properties

A SQUID magnetometer is used to characterize the magnetic behavior of these thin film bilayer structure with the applied magnetic field parallel to the plane of film. To see the nature of magnetic ordering in as-grown and hydrogenated ZnSe/Fe bilayer thin films. We have performed magnetization versus field scans at T = 2 K in a SQUID magnetometer up to a field of 30 KOe as shown in Figure 8(a). The M-H curves show that magnetic moment increases with applied field but after hydrogenation magnetic moment was found to reduce with increasing pressure of hydrogen. It may be due to hydrogen atoms combine to form molecular H_2 and in so doing, the magnetic moments are reduced, due to spins pair. Hydrogen is however diamagnetic and the same holds true for most elements. The similar results carried by Thevenard, et al. (2005) studied hydrogenation and post-hydrogenation annealing have been used as a very efficient tool to tune the hole density over a wide range, at fixed magnetic moment concentration, in thin GaMnAs layers. Reduction of the hole density resulted in strong modifications of their ferromagnetic properties.

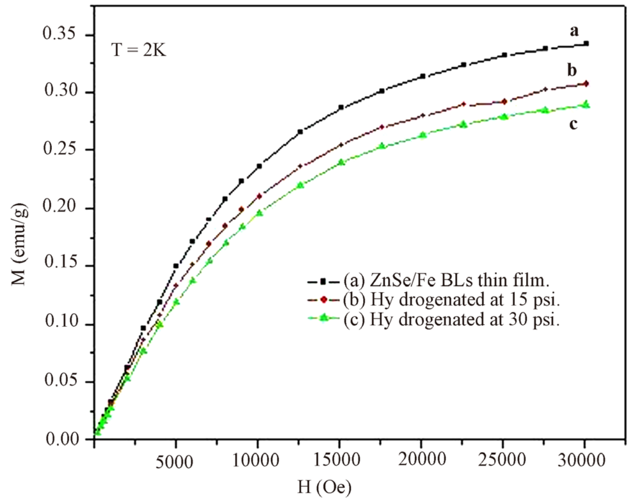


Figure 8(a)
Temperature Dependence of Magnetization (in ZFC Mode) **Under an Applied Field of 1000 Oe for As-Grown and Hydrogenated ZnSe/Fe Bilayer Thin Films**

Figure 8(b) shows the temperature dependence of the bilayer thin films before and after hydrogenation at an applied field of 1 KOe. All the data's recorded are for a net signal with drop of the magnetic contribution from the glass substrates. It was observed that ZnSe/Fe bilayer thin film showed two magnetic phases. At very low temperature up to 24 K it is showing Antiferomagnetic nature and after this at high temperature it shows ferromagnetic nature. Antiferromagnetic nature of thin film decreases with temperature up to 24 K and ferromagnetic nature increases with temperature up to 100 K and then it becomes saturate up to room temperature. Hence bilayer thin film behaves as a diluted magnetic semiconductor up to room temperature that shows magnetization does not go to zero at high temperature T and remains constant in the temperature range of 100-300 K. Similar results were carried by Pakhomov, Roberts and Krishnan (2003).

In Figure 8(b) we have also noted that phase transition in M-T curves does not change due to hydrogenation but magnetization decreases due to hydrogenation. These results similar to carried out by Liu et al. (2007) in the case of effect of hydrogenation on the ferromagnetism in polycrystalline $Si_{1-x}Mn_x$ B thin films. According them the saturation of magnetization was decreased after hydrogenation while the structural properties of films do not show any changes. Sebastian, Goennenwein, Wassner, and Martin (2004) suggested that it might be incorporation of hydrogen electrically passivated the Fe acceptor and removes the holes crucial to the wandering magnetism. They had also observed that after hydrogen passivation ferromagnetism (T_c~70 K) in $Ga_{1-x}Mn_xAs$ film prepared by low-temperature molecular beam epitaxial was disappeared.

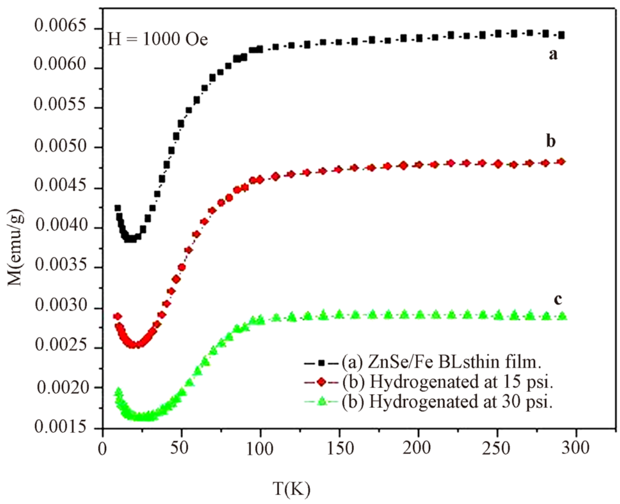


Figure 8(b)
M-H Plots of (a) As-Grown, (b) Hydrogenated at 15 psi and (c) Hydrogenated at 30 psi ZnSe/Fe Bilayer Thin Films Obtained at T = 2 K

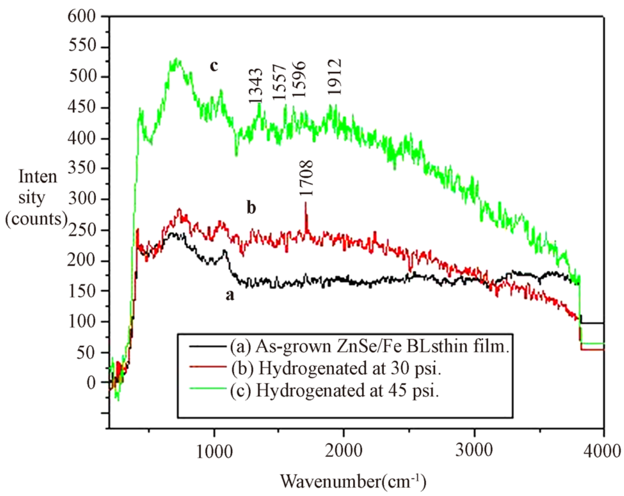


Figure 9
Room Temperature Raman Spectra of As-Grown and Hydrogenated ZnSe/Fe Bilayer Thin Films

2.8 Raman Spectroscopy

Raman spectroscopy is specially used to obtain information about the impurities of hydrogen and structural defects in the thin film structure. In Figure 9 we are going to present the plot between wave number and Raman intensity for as-deposited and hydrogenated bilayer films at different hydrogen pressure. After hydrogenation, the Raman intensity of the ZnSe/Fe belayed thin films increased. This result indicates that the crystalline quality of the ZnSe/Fe bilayer thin films were improved after hydrogenation due to the elimination of the defects, which were formed at the ZnSe/Fe hetero-interface during the growth of the ZnSe and Fe bilayers. Similar results were observed by Kim, Park, and Kim (1998) to see the effect of hydrogenation and annealing of p-type ZnSe thin films grown on GaAs (100) substrates. Due to hydrogenation a few new peaks are observed in present study on 30 psi hydrogen pressure at 1708 cm^{-1} and for 45 psi hydrogen pressure at 1348, 1551, 1596 and 1912 cm^{-1} in thin these films. Nehra et al. (2009) were also observed hydrogenation peaks in CdTe/Mn bilayer thin films with increasing hydrogen pressure. Many authors also studied the Raman spectroscopy to carry out the information about the presence of hydrogen in semi conducting materials (Vetterhoffer, et al., 1996; Pritchard, et al., 1996; Leitch, et al., 1998).

CONCLUSION

Diluted magnetic semiconductors is prepared using ZnSe/Fe bilayer structure and confirm the inter diffusion as well as the effect of hydrogenation on this structure. The XRD confirm the cubic structure of prepared thin films. The decrease in conductivity is observed in I-V characteristic measurements due hydrogen adsorption at interface or surface and accepting electron by hydrogen from DMS structure. The SQUID measurements tell us about phase changes from antiferomagnetic to ferromagnetism. The ferromagnetic behavior retains up to room temperature in these DMS films. It is also suggested that hydrogenation reduce the magnetic moment in Fe/ZnSe bilayer structure. The results clearly indicate that hydrogenation can be used to modify magnetic as well as optical properties of films. Raman spectroscopy confirms the presence of hydrogen in prepared structure.

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