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Role of hydrogen in CdTe–Mn thin film bilayer structure

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ABSTRACT

A bilayer thin film of diluted magnetic semiconductor CdTe–Mn is prepared using thermal evaporation method in Hind High Vacuum system at base pressure of 10^{-5} Torr. The samples are annealed in atmospheric condition at constant temperature of 400 °C for 1 h. Then the hydrogen gas is introduced at different pressure (0–45 psi) for 30 min to hydrogenate these films at room temperature. The optical band gaps of CdTe–Mn bilayer thin films are found to increase with increasing pressure of hydrogen. Therefore it may be suggested that optical band gap can be tailored by introducing hydrogen in CdTe–Mn bilayer thin film. Raman spectra of these samples shows increasing intensity of peaks with hydrogenation and one predominant peak is observed at 336.47 cm^{-1} that shows the clear evidence of presence of hydrogen in sampled at room temperature. The optical micrographs of these samples show morphological variations due to the hydrogenation.

1. Introduction

Most of the semiconductor material are diamagnetic by nature and therefore cannot take active part in the operation of the magneto electronic devices. In order to enable them to be useful, a recent effort has been made to develop diluted magnetic semiconductors (DMS) in which small quantity of the magnetic ion is introduced into semi-conductor [1]. Magnetic semiconductors are very important materials in the current electronic industries [2]. Diluted magnetic semiconductors are expected to play an important role in interdisciplinary material science and electronics because charge and spin degrees of freedom accommodated into a single material exhibits interesting magnetic, magneto-optical, magneto-electronic and other properties [3–7]. Diluted magnetic semiconductors are compound of alloy semiconductor containing a large fraction of magnetic ions [8].

In recent years, II–VI compound semiconductors are attracting a great deal of attention because of their potential abilities in a wide spectrum of optoelectronic devices [9]. Among the growth techniques for large area and low cost CdTe thin film, the vacuum evaporation method is often preferred due to the large possibility to modify the deposition conditions [10–12]. In order to obtain efficient CdTe/Mn bilayer by this technique, a high growth temperature during the deposition of CdTe thin film is necessary. Hydrogen strongly affects the electronic properties of materials and interstitial hydrogen is a fast diffuser in semi-conducting materials. It can bind to native defect or other impurities, often eliminating their electrical activity—a phenomenon known as passivation. Electrical and optical measurements such as current/voltage provide detailed information about the electronic effects of hydrogen. A "universal alignment" model successfully describes the electronic behavior of hydrogen in a wide range of materials and allows for prediction for materials in which the role of hydrogen is yet to be explored [13,14].

Recently it has been observed that hydrogen can tune the optical band gap of $In_xGa_{1-x}As_{1-y}H_y$, an innovative semi-conducting alloy of high potential material for telecommunications and solar cell applications [13,14]. In XRD measurements sharp diffraction peaks was observed at 23.73°, 39.27°, 46.43°, 56.79° and 62.40° corresponding to (1 1 1), (2 2 0), (3 1 1), (4 0 0) and (3 3 1) planes of the cubic structure [15]. Optical band gap calculation has been carried out on the basis of Tauc relation [16]. The electronic passivation of host impurities induced by atomic hydrogen in semiconductor reported by Pankove et al. [17]. They suggested that hydrogen play an amphoteric role since it can neutralize either donors, acceptors or activate neutral impurities. Both forward and reverse currents were decreased with increasing hydrogen concentration caused by the increase of barrier height at the interface [18]. According to them, the dramatic increase in resistance and the increase in Schottky barrier capacitance were due to reduction of free charges carriers after hydrogenation. Electrical study was carried out in semiconductors by Corbett et al. [19] and pointed out that hydrogen neutralizes defects at relatively low temperatures because hydrogen is very mobile at low temperatures.

The study of hydrogen in semiconductors started more than 50 years ago, when Mollow [20] observed that the exposure of hydrogen on ZnO caused a marked increase in conductivity of the

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material. In the 1980s came a real explosion of activity when Haller et al. [21,22] showed that hydrogen in germanium could passivate electrically active impurities but also activate iso-electric impurities that are normally electrically inactive. The Raman studies was carried out in semiconductor and rare earth metal hydrides [23–28] for detection of the presence of hydrogen and *I–V* characteristic was carried out [29] to see the response of hydrogen on Pt-GaN Schottky diodes. Noble character of hydrogen gas is the most abundant element in the universe and also omnipresent and easily incorporated in metals and semiconductors. In the present study we are carried out the role of hydrogen to see the effect on optical properties and vibration mode changes in Raman spectroscopy studies.

2. Experimental

The samples of CdTe/Mn bilayer thin films are prepared by thermal evaporation method (resistive heating) using vacuum coating unit at a pressure of 10^{-5} Torr on well cleaned glass substrate. Compound cadmium telluride (99.99% purity) and Mn element (99.98% purity) in granules form are procured from Alfa Aesar, Jonson Matthay Company, U.S.A. and are used for deposition. The normal distance of source from substrate is kept at 6 cm to deposit uniform thin film structure. The bilayer structure of CdTe/Mn thin films are deposited one by one material evaporation. The thickness of CdTe/Mn bilayer thin films is 200 nm (100 nm CdTe and 100 nm Mn) as measured by quartz crystal thickness monitor as well as gravetric method.

These films are annealed at constant temperature of 400 °C for 1 h in atmospheric conditions to get homogeneous structure and interdiffusion of bilayer of CdTe–Mn. These samples are kept in hydrogen chamber at room temperature, where hydrogen gas is introduced at different pressure for 30 min.

X-ray diffraction (XRD) have been taken by using Panalytical System having Cu Kα, as a radiation source of wavelength λ = 1.0425 Å with scan speed 0.5° per minute in the range 15–70° for the determination of structure. The analysis has performed by using power X-ray software program. The transmission spectra of as deposited and annealed hydrogenated thin films are carried out in the wavelength range 400–800 nm with the help of Hitachi Spectrophotometer Model-330. The optical micrographs are also taken with the help of Lamode optical microscope at 10× magnification having resolution of the order of 1 μm and the microscope is kept in reflection mode. The Raman spectra of samples were recorded at different pressure of hydrogen using Green laser beam of wavelength 532 nm. (Raman model-3000 system).

3. Results and discussion

3.1. Structural characterization of CdTe/Mn bilayer structure

Fig. 1 shows the X-ray diffraction pattern for as deposited CdTe/Mn bilayer thin films structure. The diffraction peaks are observed at 2θ angles of 23.77°, 39.38°, 46.48° and 62.37° correspond to (1 1 1), (2 2 0), (3 1 1) and (3 3 1) planes of the cubic symmetry of CdTe structure. The lattice constant is found to be *d* = 6.4702 and agree well with Rusu and Rusu [10]. No other diffraction peaks associate with metallic Te, Mn and other compounds are observed indicating that respective bilayered structure present a single phase with highly oriented CdTe crystallites.

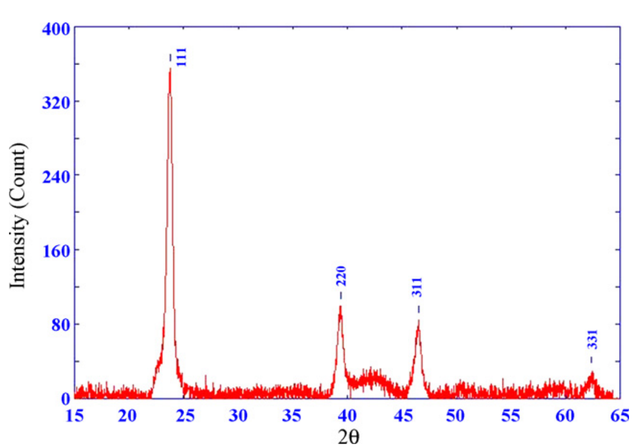

Fig. 1. XRD for as deposited CdTe–Mn bilayer thin film.

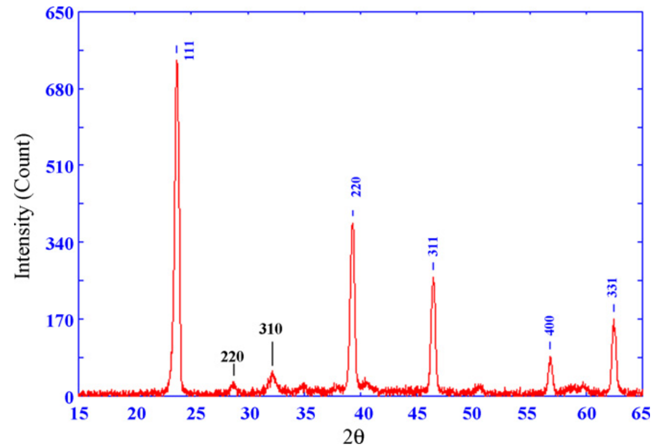

Fig. 2. XRD for annealed CdTe–Mn bilayer thin film.

Fig. 2 shows a dramatic change in the X-ray diffraction spectra of annealed CdTe/Mn bilayer thin film at 400 °C for 1 h in air. The sharp diffraction peaks are observed at 23.73°, 39.27°, 46.43°, 56.79° and 62.40° corresponding to (1 1 1), (2 2 0), (3 1 1), (4 0 0) and (3 3 1) planes of the cubic structure and agree well with [15]. One can observe the clear difference between as deposited and annealed spectra. In the annealed spectra we get the additional peaks of Mn observed at 28.69° and 32.19 corresponding to (2 2 0) and (3 1 0) respectively having lattice constant *d* = 8.86, which confirms the mixing of Mn in semiconductor. The intensity of all the diffraction peaks is increased due to possibility of grain growths. Grain sizes for as-grown samples are found to be less in comparison to annealed samples.

3.2. Optical properties of CdTe/Mn bilayer structure

Fig. 3 shows transmission with wavelength of as-deposited and annealed hydrogenated CdTe/Mn thin films at different pressure of hydrogen. The transmission spectra of as-deposited sample shows higher transmission than the vacuum annealed and hydrogenated samples and it was also noted that transmission is found to be decreased with increasing pressure of hydrogen. These variations

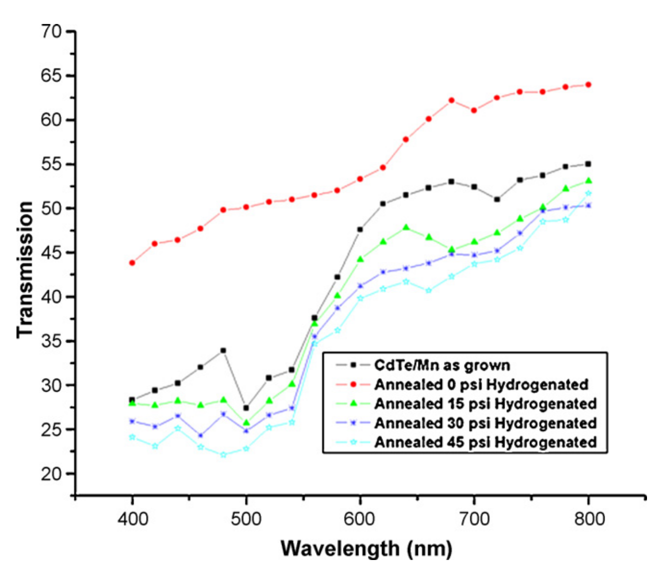

Fig. 3. Wavelength vs. transmission plot for CdTe–Mn bilayer thin films.

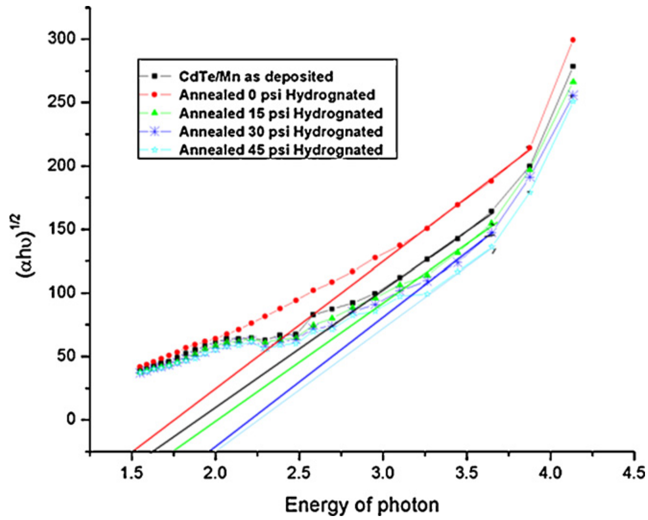

Fig. 4. Optical band gap of CdTe–Mn bilayer thin films.

in the transmission spectra are due to the defect removal and intermixing of samples by virtue of annealing and hydrogenation.

The optical band gap of CdTe/Mn thin films have been calculated using the relation [16]

$$\alpha h\nu = A(h\nu - E_g)^m,$$

where A is edge parameter or constant. E_g is the band gap of the material and m determines the type of transition, $m = 0.5$ for direct band gap material and $m = 2$ for indirect band gap material. The energy band gap E_g is estimated from studies by plotting $(\alpha h\nu)^2$ vs. photon energy ($h\nu$). Fig. 4 shows the variation of optical band gap with hydrogen pressure. The optical band gap is found to increase with increasing pressure of hydrogen. The band gap of as-grown sample is found to vary from 1.5 to 1.9 eV with hydrogenation. This agrees well with Rusu and Rusu [10] for optical behavior of multilayered CdTe/Cu thin films deposited by stacked layer method. In our case results are slightly different due to the bilayer and magnetic element Mn. It is found that the band gap for as grown sample is lower than the annealed hydrogenated samples and then it increases with increasing pressure of hydrogen. It may be due to the hydrogen accumulation at interface that was responsible for the modification of band gap. It was suggested that hydrogen tailored the optical band gap. The result related to the hydrogen accumulation at the interface was confirmed by Singh [30]. The electronic passivation of host impurities induced by atomic hydrogen in semiconductor agrees well as reported by Pankove et al. [17]. They suggested that hydrogen play an amphoteric role since it can neutralize either donors or acceptors, or activate neutral impurities.

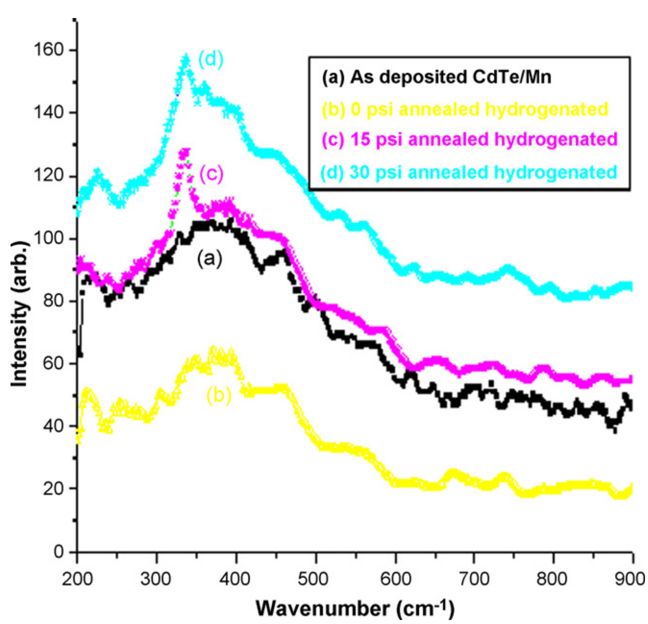

Fig. 5. Raman spectra of CdTe–Mn bilayer thin films for different hydrogen pressure.

3.3. Raman spectra

Raman spectroscopy is specially used to obtain information about the impurities of hydrogen and structural defects in the thin film structure. In Fig. 5, we present the plot between wave number and Raman intensity for as-deposited, annealed and hydrogenated bilayer films at different pressures. Raman spectra of these samples shows that the intensity of annealed sample decreases, but for annealed hydrogenated samples, it increases due to the absorption of hydrogen in these samples and one extra peak at 336.47 cm^{-1} is observed in Raman spectra after hydrogenation by us. This suggests the presence of hydrogen in these samples. The direct observation of hydrogen molecules in semiconductors was reported, first time with Raman spectroscopy in GaAs [25] and shortly their after in silicon with infrared absorption spectroscopy [26] as well as Raman spectroscopy [27]. The experimental results produced remarkably large shift of the vibration frequency. Computational

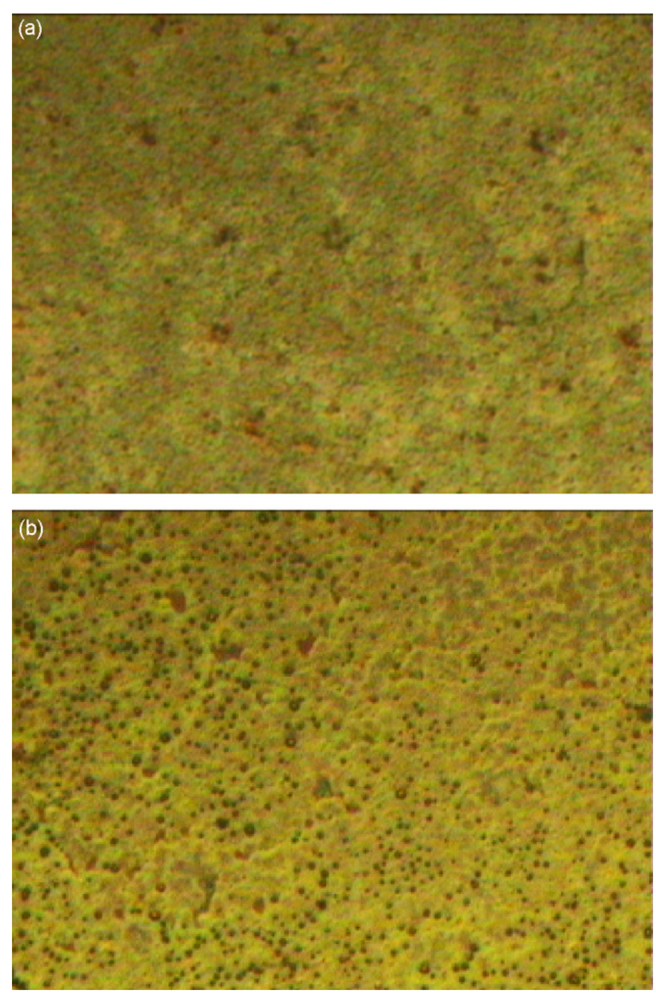

Fig. 6. Optical photographs (a) annealed and (b) annealed hydrogenated at 45 psi.

studies confirmed that the interaction between hydrogen and semiconductor are quite strong. Authors Kim et al. [23] carried out Raman spectroscopy for P type ZnSe thin films grown on GaAs substrate and observed increase in intensity with hydrogenation at room temperature well agree with our results increasing intensity of peaks with hydrogenation. In case of ZnO nanoparticles intensity was found to decrease with hydrogenation but they were unable to detect hydrogen related local vibrational modes [24].

3.4. Surface morphology

Fig. 6a and b shows optical microscope surface morphology of bilayer thin films structure in reflectance mode with and without hydrogenation. We have noted the variation of surface morphology with hydrogen pressure. One can see the clear difference between the photographs, which also shows the presence of hydrogen in films. In this paper we present only 45 psi hydrogenated films for contrast with virgin films.

4. Conclusion

In this paper we discuss about the XRD of CdTe/Mn structure and observed that mixing of Mn for formation of dilute magnetic semiconductors. The variation in optical band gap in as-deposited and annealed films also confirms the mixing of Mn. We have also observed the effect of pressure of hydrogen on optical band gap and suggest that hydrogen modified the optical band gap of CdTe/Mn thin films with hydrogenation. It is suggested that the passivation of semiconducting films by hydrogen is responsible for modification of optical band gap. The Raman spectra confirm the presence of hydrogen in these films.

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