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# Surface modification of thermally evaporated CdTe thin films for sensing application of organic compounds

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The study involves the growth of bulk cadmium telluride (CdTe) by using vertical directional solidification (VDS) technique. The as grown CdTe compound has been used as a source material to deposit thin films onto glass substrates at room temperature by thermal evaporation technique under high vacuum conditions of $10^{-5}$ mbar. The thickness of film has been measured around 310 nm. Characterization of bulk CdTe compound and its thin films have been done by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) and photoluminescence (PL) techniques. CdTe thin films have been then used for exposure to vapors of organic compounds such as acetone, formaldehyde, methanol, ethanol, benzene, toluene and chloroform in order to ascertain the use of these films for various sensors. The optical and micro structural properties of CdTe thin films have been studied using PL and AFM techniques so as to evaluate the sensing capabilities of CdTe thin film towards specific compounds which have been used for exposure.

**Keywords:** VDS technique, Thermal evaporation, Sensing, AFM, PL

## 1 Introduction

Cadmium telluride (CdTe) is a direct band gap semiconductor material with an energy gap of 1.45 eV and is therefore well suited for efficient conversion of solar light into electricity. Of the II–VI semiconductors, CdTe is the best established from the standpoint of applications. Its bandgap is ideal for solar cells applications as it coincides with the solar spectrum. It is also widely used as a buffer layer in infrared detectors utilizing HgCdTe as the sensor element. CdTe, by itself, can be used as a sensor material for gamma and X-rays detectors. More recently, it has been considered for optical waveguides applications that take advantage of its exceptional non-linear properties. It is also of great interest to the field of nanotechnology as CdTe nanoparticles have been shown to photoluminescence at different frequencies depending on the size of the nanoparticles[1,2].

Crystal growth of CdTe was pursued by the modified bridgman technique. The main advantage of this technique is that the composition of the melt can be controlled. It also offers the advantages of uniformity of ingot size and greater uniformity of impurities in the direction transverse to the direction of growth. Crystals of CdTe can be grown stoichiometrically, cadmium-rich, or tellurium-rich, by changing the pressure of one of the components[3].

CdTe is of continuing promising contenders for use in a large scale for the thin film devices technology, i.e., solar cells, IR and γ detectors, field effect transistors etc. From the methods used for the preparation of CdTe films, the thermal evaporation in vacuum is often preferred because it offers large possibilities to modify the deposition conditions and so to obtain films with determined structure and properties. One of the preparation methods, which use the thermal evaporation in vacuum, is the quasi-closed volume technique. It permits to change the deposition conditions by varying the temperature of both the substrate and evaporation source and also by the modification of the shape and the volume of the chamber, which delimit the deposition space. Using such a deposition technique, we have obtained both the textured and quasiamorphous CdTe films. It was found that the structure strongly influences the electrical and optical properties of the films[4].

Semiconductor quantum dots (QDs) of CdTe have great application potential in the field of biosensors due to their excellent optical property and large specific surface area, which is easily accessible to the analytes. However, QDs, themselves, do not have

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specific recognition toward the detected objects. Therefore, different types of biomolecules, including protein, enzyme, and DNA, are conjugated with QDs to form nanocomposites either in solution or on the substrate surface in order to offer selectivity of biosensors. Although numerous physical or chemical strategies have been successfully applied to develop new nanocomposite biosensors, several disadvantages, for example, time and cost consumption, difficulty of large-scale production, and absence of universality, limits the practical applications of these methods. The electrostatic layer-by-layer (LBL) self-assembly technique introduced by Decher, which is based on the alternative deposition of opposite-charged species on the substrates, may provide an alternative way to develop new generation of nanocomposite biosensors. The simplicity, economy, universality, and friendly environment of film fabrication by LBL have contributed to the widespread popularity of this method. Previous studies on the LBL multilayers have demonstrated that the optical, electrical, and electrochemical response of nanoparticles in the multilayer film could be tailored through the layer architecture[5,6].

A gaseous formaldehyde sensor based on CdTe QDs/polyelectrolyte multilayer film (QDMF) was fabricated. It presents gaseous formaldehyde detection by utilizing CdTe QDs. During sensor constructing process, CdTe QDs and PDDA were deposited alternately to form QDs multilayer films by LBL method and bovine serum albumin (BSA) was deposited on the outermost layer for reducing interference from other organic molecules. Gaseous formaldehyde can be detected via its quenching effect on the PL intensity of the QDMF. The influence of the co-existed gases was also investigated in this study. The QDs-multilayer films provided a convenient, low-cost, and sensitive method for gas detection, which could be an alternative technique in the potential application of the harmful volatile organic compounds (VOCs) gas-analysis[7].

The purpose of the present work is to study the effect of various chemicals on the micro structure and optical properties of CdTe thin films deposited onto glass substrates. The main aim of this work is to synthesize the CdTe thin films at different substrate temperatures and different film thicknesses using thermal evaporation technique and to characterize these films for their elemental compositional analysis and micro structural properties. Later, these films were exposed to various chemical compounds namely, formaldehyde, acetone, toluene, benzene, methanol, ethanol and chloroform. The vacuum evaporation method is used to synthesize CdTe thin films as it has advantages over other deposition techniques. The thin films synthesized by this technique are uniform homogeneous, more adhesive to the substrates and compact. The amount of impurities included in the deposited layer are found to be minimized, the tendency to form oxides will be considerably reduced as the films are deposited under high vacuum conditions.

## 2 Experimental Details

Cadmium telluride (CdTe) bulk compound was grown by vertical directional solidification (VDS) technique[8]. It is difficult to prepare stoichiometric thin films using layer by layer deposition of different elements (Cd and Te); hence the films were prepared using as grown CdTe compound as the source material for thermal evaporation under high vacuum conditions of $10^{-5}$ mbar. Liquid $N_2$ trap was used to avoid anti contamination during the evaporation of the source material.

The films of the as grown bulk CdTe compound were deposited onto glass substrates at room temperature. The thickness of the film is kept about 310 nm. Powder X-ray diffractometer (Miniflex 600, make Rigaku), scanning electron microscopy (SEM ZEISS EVO MA-10), energy dispersive spectroscopy (EDS Oxford Link ISIS 300), atomic force microscopy (AFM multimode, nanoscope V, make Veeco instruments) and photoluminescence (PL model Perkin Elmer LS 55) techniques were used for characterizing the bulk and CdTe thin films. The thickness measurement of CdTe thin film was carried by using Dektak 150 surface profiler. Carrier type measurement of the as grown CdTe compound has been carried out by the hot probe method.

Thin films of CdTe were exposed to vapors of various organic compounds such as, acetone, formaldehyde, benzene, toluene, chloroform, methanol and ethanol. 100 mL of organic compound were taken each in different beakers and conical flasks for exposure to the films for 4 h. Continuous stirring of the organic compound was enabled through a magnetic stirrer so that the heat distribution is uniform. A copper/constantan thermocouple was used to measure the actual temperature of the organic compound while heating. The photoluminescence spectra (PL) of the exposed films were recorded on the same day of exposure to the organic compound and next day also to observe the variation in the PL spectra. Scanning probe microscope (SPM) was used to investigate the microstrucural behavior of the thin films exposed to various organic compounds. Later, the sensing abilities of CdTe thin films towards acetone and formaldehyde were studied in detail varying the exposure durations from 1 h to 4 h. A photograph of experimental setup is shown in Fig. 1.

## 3 Results and Discussion

### 3.1 CdTe bulk compound

Carrier type measurement of the as grown CdTe bulk compound reveals the *p*-type carriers. The X-ray diffraction pattern (Fig. 2) shows presence of very sharp and well resolved peaks of single phase CdTe bulk compound having cubic structure with polycrystalline nature[9,10]. The results are in good agreement with JCPDS File No. 15-0770. Among all planes (220) and (111) have maximum intensity which shows the quantitative growth of bulk compound along these planes. As given in Table 1, average crystallite size along these planes has values 43, 41 nm, respectively. SEM micrograph in Fig. 3(a) indicates the presence of set of cleavage planes revealing the formation of ordered structure of CdTe compound. Elemental compositional analysis of the as grown compound shown in Fig. 3(b) revealed that the stiochiometry of Cd and Te is maintained throughout the compound after growth and no other element as an impurity is present. Figure 4 shows the photoluminescence spectras of CdTe bulk compound at excitations of 345 nm and 374 nm, respectively. It can be seen that the PL emission wavelength of bulk CdTe is around 630 nm and 670 nm when excited at wavelengths of 345 nm and 374 nm, respectively. Band gap calculated are 1.8 eV and 1.9 eV for excitations of 345 nm and 375 nm, respectively. Band gap increases for nano structured material as surface to volume ratio increases and electronic excitation levels also vary for nano materials.

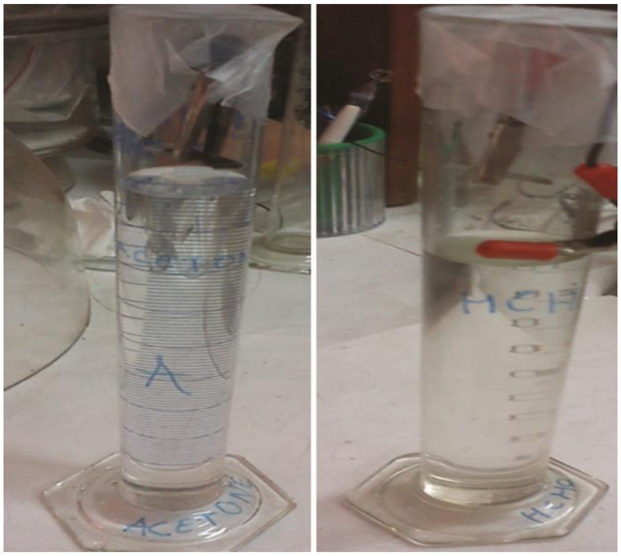

Fig. 1 — Experimental set up of exposure of CdTe thin film to acetone and formaldehyde vapors.

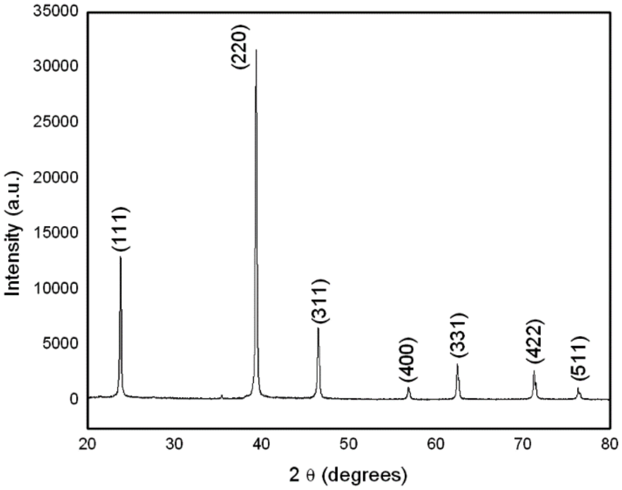

Fig. 2 — XRD pattern of CdTe bulk compound.

### 3.2 CdTe thin films

Figure 5 represents the XRD patterns of CdTe thin films deposited at room temperature (RT) which show polycrystalline nature of growth. Planes along (*hkl*) indices, (111), (220) and (311) revealed the formation of single phase cubic structure of CdTe (JCPDS File No. 75-2083). The crystallite size calculated by using Scherer formula is given in Table 2. SEM micrograph of CdTe thin film grown at RT shown in Fig. 6(a) reveals that the surface of the film shows some islands like morphology at some of the locations on the substrate. The particles are very small in size in the range of 55– 80 nm. Figure 6(b) shows the energy dispersive spectrometer **(**EDS**)** pattern of the corresponding area of the CdTe thin film indicating the presence of stoichiometric Cd and Te along with the peaks of substrate materials, i.e., O, Na, Mg, Si and Ca.

The photoluminescence (PL) spectra of CdTe thin films grown on glass substrates have been obtained at

Table 1 — Crystallite size of CdTe bulk material crystal phase

| Crystal plane | (1 1 1) | (2 2 0) | (3 1 1) | (4 0 0) | (3 3 1) | (4 2 2) | (5 1 1) |
|---|---|---|---|---|---|---|---|
| Crystallite size (nm) | 41 | 43 | 38 | 36 | 18 | 19 | 12 |

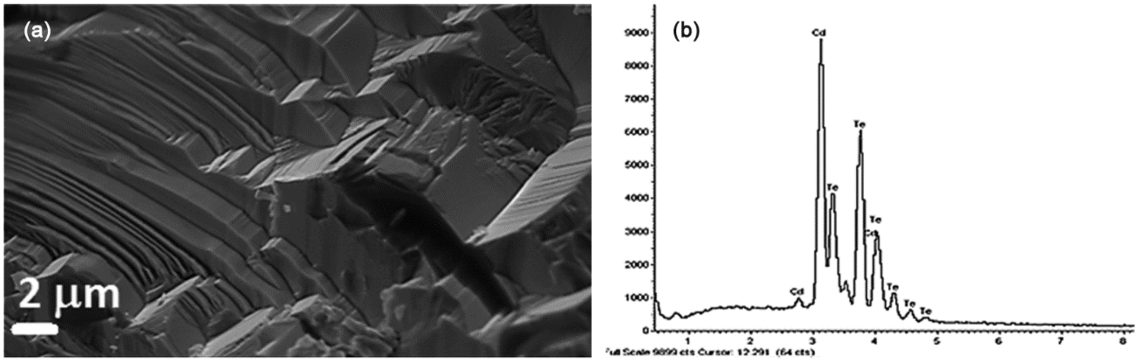

Fig. 3 — (a) SEM micrograph of CdTe bulk compound (b) its EDS pattern.

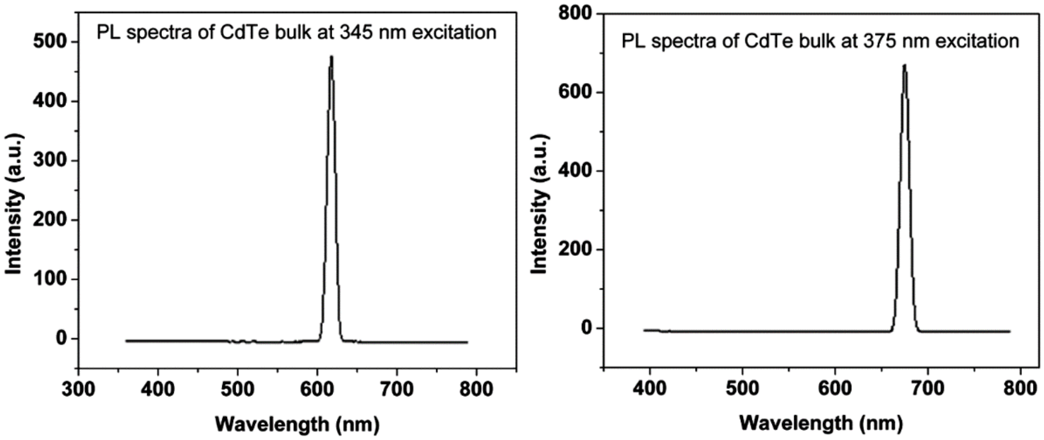

Fig. 4 — PL spectra of CdTe bulk compound at excitations of 345 nm and 375 nm.

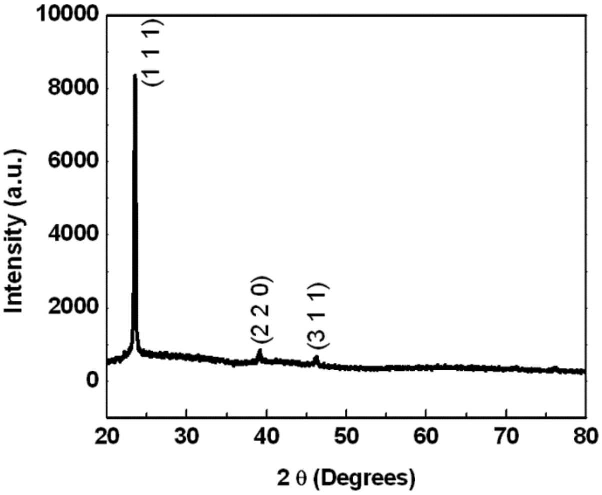

Fig. 5 — XRD pattern for CdTe thin films deposited at RT.

Table 2 — Crystallite size of crystal planes of CdTe thin films

| Crystal plane | (1 1 1) | (2 2 0) | (3 1 1) |
|---|---|---|---|
| Crystallite size (nm) | 23 | 38 | 27 |

an excitation of 316 nm. From the Fig. 7, a decrease in the intensity of CdTe thin film from the intensity of CdTe bulk material was observed. It may be due to the fact that smaller nanoparticles penetrate the metastable states of electronic excitation of a thin film and increase the inter-particle energy transfer opportunities within the layers. The optical band gap was determined using the formula $E_g$ = 1241/$\lambda$ (nm). The band gap calculated was found to be 2.2 eV.

The surface morphology and surface roughness (Table 3) were determined by atomic force microscopy (AFM). Thin films of CdTe were investigated in tapping mode of AFM. As depicted in the AFM image in Fig. 8(a), the particle size was found to be in the range of 40 – 70 nm and roughness is recorded as 3.69 nm over an area of 2 μm. The particle size of CdTe thin films as observed under AFM are in good agreement with SEM results.

### 3.3 Exposure of CdTe thin films to vapors of various organic compounds

#### *3.3.1 Photoluminescence analysis*

The photoluminescence (PL) spectra have been recorded at an excitation of 358 nm.

(i) Methanol exposure: As shown in Fig. 9(a), when CdTe thin film was exposed to methanol, same

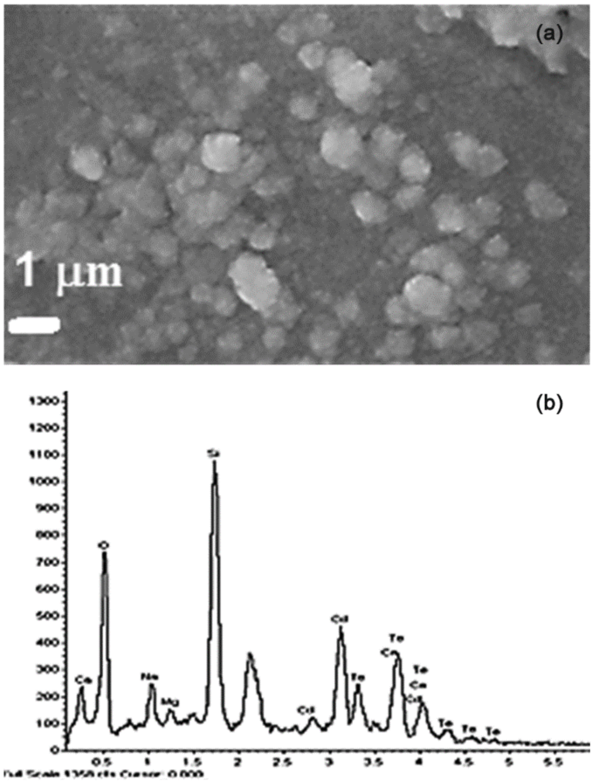

Fig. 6 — (a) SEM micrograph of CdTe thin film deposited at RT and (b) its EDS pattern.

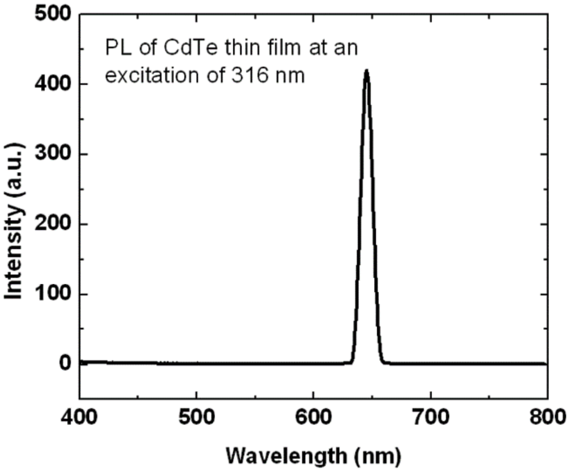

Fig. 7 — Photoluminescence spectra of CdTe thin films.

day PL spectra was recorded and showed that the intensity of the peak is less than that of CdTe unexposed film. A red shift was also observed. When PL was recorded on the next day, a very intense peak was seen as shown by the green colored curve in the PL spectras. This phenomenon may arise due to degradation of surface of CdTe thin film after exposure to methanol. This degradation effect was also seen in the AFM analysis as the surafce of the thin film exposed to methanol shows more roughness than the thin film which was unexposed to methanol.

Table 3 — Roughness data for CdTe films unexposed and exposed to various organic compounds

| S. No. | Chemical compound used for exposure | Roughness (*Ra*) of unexposed CdTe thin film (nm) | Roughness (*Ra*) of exposed CdTe thin film (nm) |
|---|---|---|---|
| 1 | Methanol | 3.20 | 2.80 |
| 2 | Ethanol | 3.20 | 2.69 |
| 3 | Benzene | 3.20 | 5.67 |
| 4 | Toluene | 3.20 | 6.18 |
| 5 | Chloroform | 3.20 | 2.73 |
| 6 | Formaldehyde | 3.20 | 3.10 |
| 7 | Acetone | 3.20 | 3.10 |

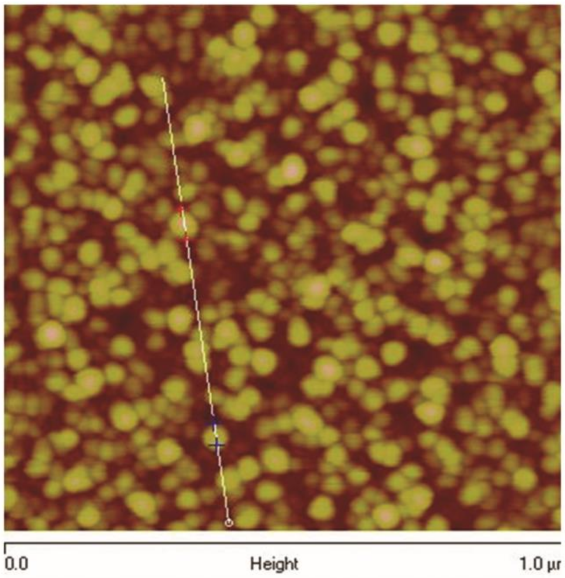

Fig. 8 — AFM image of CdTe deposited at RT.

(ii) Ethanol exposure: After exposure, PL spectra were recorded on the same day, a high intensity peak around 1000 a.u. was observed as depicted by the red curve in Fig. 9(b). The PL spectra recorded next day after exposure showed no significant difference from the PL spectra recorded on the same day of exposure. Exposure to ethanol of the CdTe thin film has been degraded.

(iii) Toluene exposure: Same day PL showed that the intensity of the peak was less than that of CdTe unexposed film. A red shift was also observed as seen in Fig. 9(c). When PL was recorded the next day, a very intense peak was seen as shown by the green colored curve in the PL spectras.

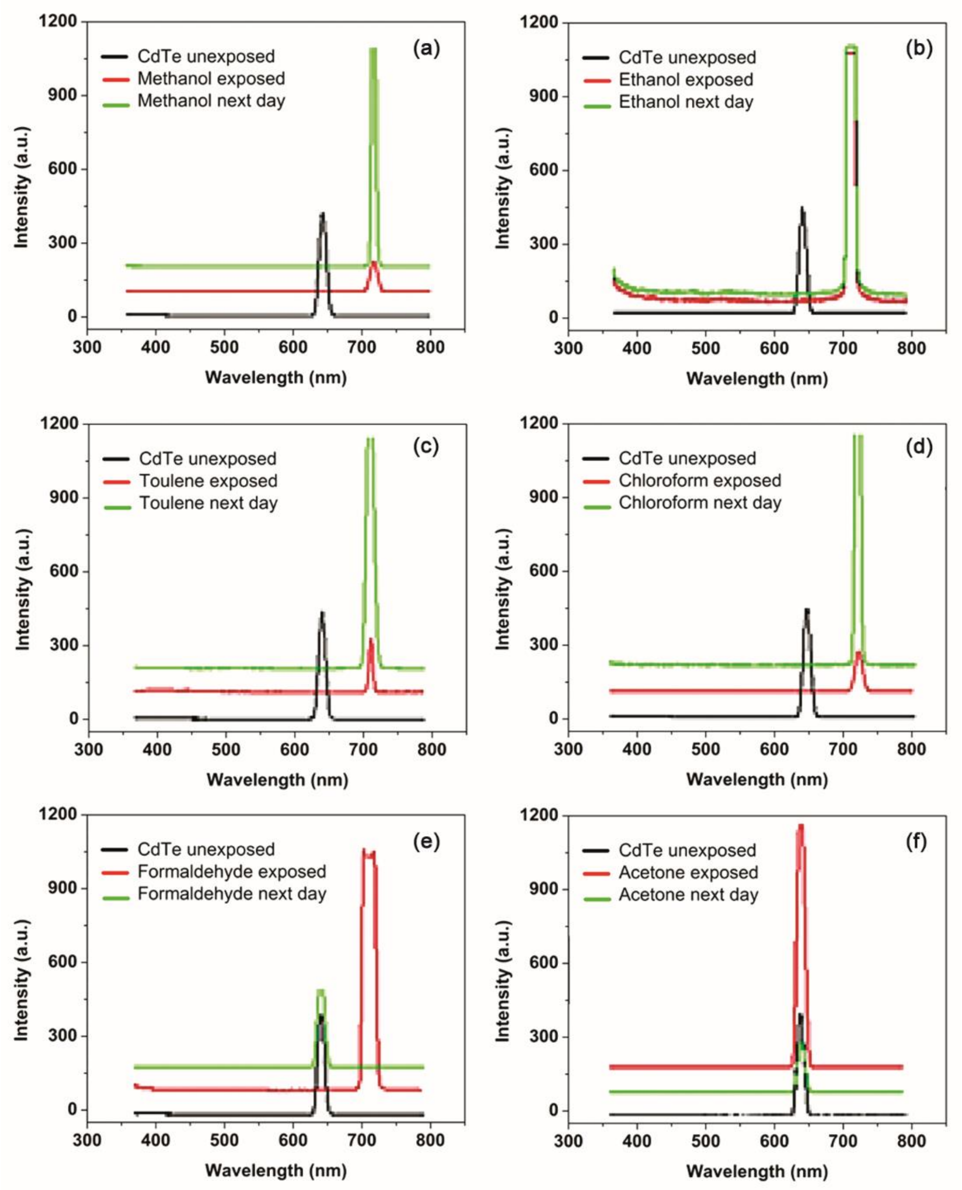

Fig. 9 — Photoluminescence spectra of CdTe thin film exposed to (a) methanol, (b) ethanol, (c) toluene, (d) chloroform, (e) formaldehyde and (f) acetone.

This phenomenon may arise due to degradation of CdTe thin film after exposure to toluene.

(iv) Benzene exposure: It showed similar results as toluene.

(v) Chloroform exposure: It showed similar results as toluene, Fig. 9(d).

(vi) Formaldehyde exposure: When PL spectra were recorded on the same day after formaldehyde exposure, a very high intensity peak of 1100 a.u. was observed along with a red shift shown in Fig. 9(e). PL recorded next day showed that the peak was identical to the peak of unexposed CdTe with the same intensity and wavelength. This result has also been confirmed by AFM analysis as the roughness were identical for CdTe unexposed and CdTe exposed to formaldehyde. It can be concluded here that CdTe thin film can be used as a formaldehyde sensor as we can regain the film structure after formaldehyde exposure.

(viii) Acetone exposure: When PL spectra were recorded on the same day after acetone exposure, a very high intensity peak of 1000 a.u. was observed along with a red shift as shown in Fig. 9(f). PL recorded on next day showed that the peak wais identical to the peak of unexposed

CdTe with the same intensity and wavelength. This result has also been confirmed by AFM analysis as the roughness are identical for CdTe unexposed and CdTe exposed to acetone. It can be concluded here that CdTe thin film can be used as an acetone sensor as we can regain the film structure after acetone exposure.

### *3.3.2 Atomic force microscopy analysis*

(i) Methanol exposure: As shown in Fig. 10(b), roughness of CdTe thin film which is not exposed to methanol is 3.20 nm over an area of 3 µm and roughness of CdTe thin film after exposure to methanol is 2.80 nm over an area of 3 µm. AFM analysis thus shows that the film surface is not totally recovered after exposure to methanol. CdTe thin film cannot be used as a methanol sensor as we are not able to recover the surface of the film after exposure to methanol.

(ii) Ethanol exposure: Roughness of CdTe thin film which was not exposed to ethanol is 3.20 nm over an area of 3 µm and roughness of CdTe thin film after exposure to methanol is 2.69 nm over an area of 3 µm. It can be seen here in Fig. 10(c) that ethanol has damaged the surface of the CdTe thin film and the film surface is not recoverable after ethanol exposure.

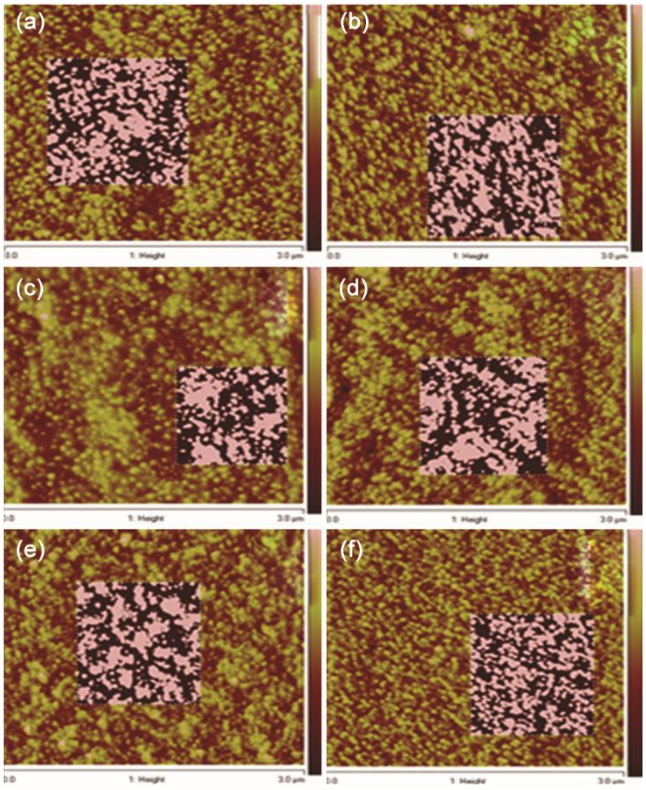

Fig. 10 — Roughness images of CdTe thin film (a) unexposed, (b) film recovered after exposure to methanol, (c) ethanol, (d) chloroform, (e) formaldehyde and (f) acetone.

(iii) Benzene, chloroform and toluene exposure: It showed similar degradation like ethanol and methanol. Thus CdTe cannot be used as sensor for these compounds (Fig. 10(d))

(iv) Formaldehyde exposure: Figure 10(e) shows roughness of CdTe thin film which was not exposed to formaldehyde that is 3.20 nm over an area of 3 µm and roughness of CdTe thin film after exposure to formaldehyde is 3.10 nm over an area of 3 µm. The roughness data for both the images are nearly equal and the film surface also shows resemblance. AFM analysis thus shows that CdTe thin film can be used as a formaldehyde sensor as the CdTe film is recovered after exposure to formaldehyde. This data matches with the results obtained in PL spectra discussed earlier.

(v) Acetone exposure: Roughness of CdTe thin film which was not exposed to acetone is 3.20 nm over an area of 3 µm and roughness of CdTe thin film after exposure to acetone is 3.10 nm over an area of 3 µm as shown in Fig. 10(f). The roughness data for both the images are nearly equal and the film surface also shows resemblance. AFM analysis thus shows that CdTe thin film can be used as an acetone sensor as the CdTe film is recovered after exposure to acetone. This data matches with the results obtained in PL spectra discussed earlier.

Figure 11 shows the PL spectras of CdTe thin film exposed to acetone for durations varying from 1 h to 4 h. The presence of acetone cannot be detected when the film is exposed for durations of less than1 h. When CdTe thin film is exposed to acetone vapors for two hours and more, an intense peak arises which marks the detection of acetone vapors. PL recorded after 3 days shows that the peak is identical to the peak of unexposed CdTe with the same intensity and wavelength.

Figure 12 shows the PL spectras of CdTe thin film exposed to formaldehyde for durations varying from 1 h to 4 h. In all figures from 12(a-d), detection of formaldehyde vapors is shown by an intense red peak along with a shift toward higher wavelength. PL recorded after 3 days shows that the peak is identical to the peak of unexposed CdTe with the

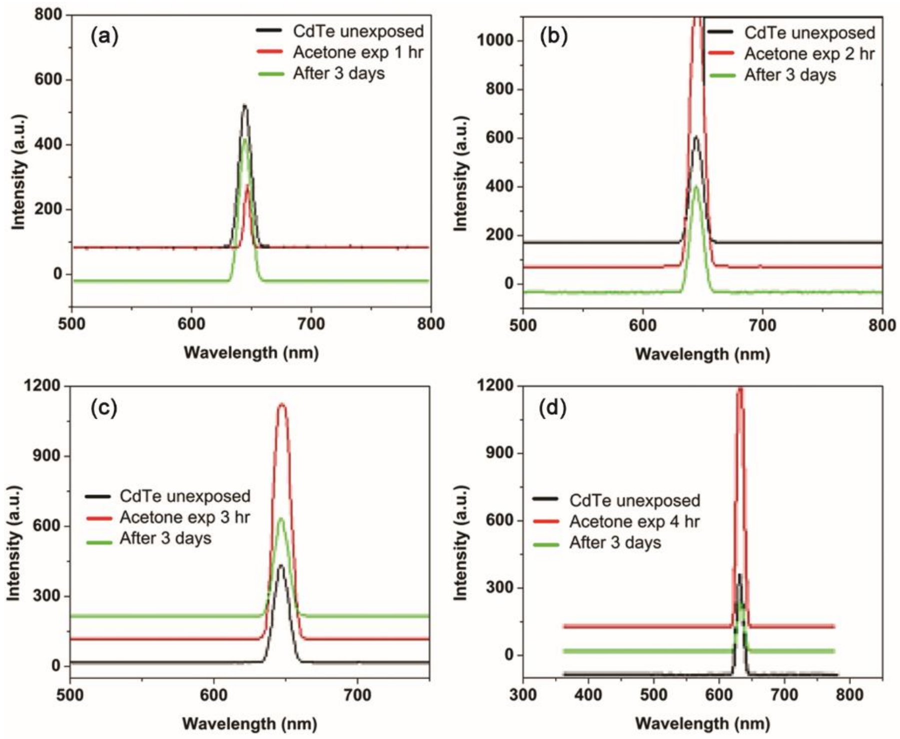

Fig. 11 — PL spectra of CdTe thin film exposed to acetone (a) 1 h of exposure, (b) 2 h of exposure, (c) 3 h of exposure and (d) 4 h of exposure.

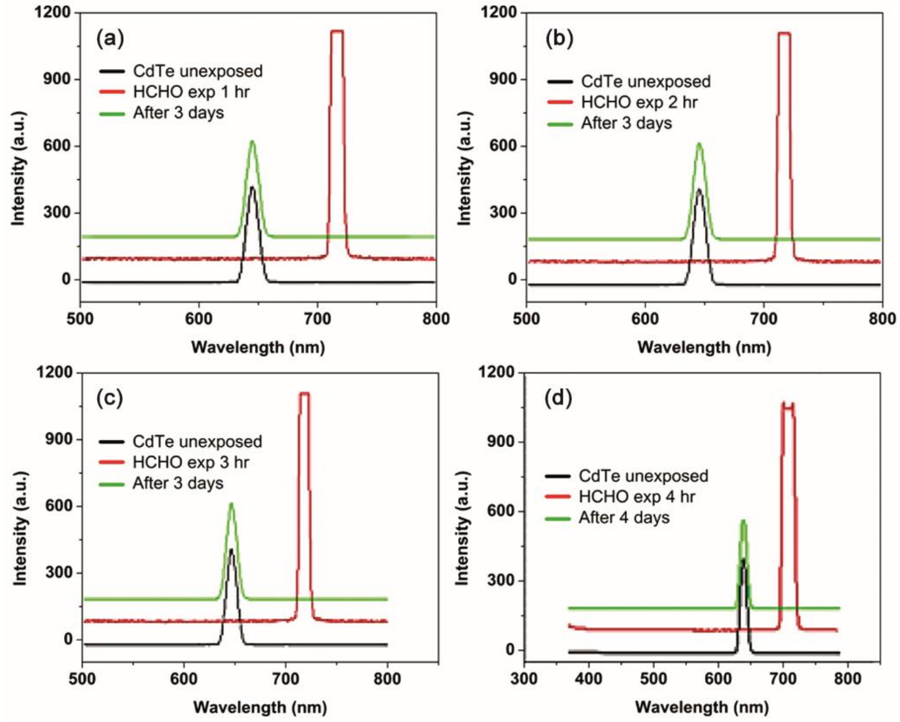

Fig. 12 — PL spectra of CdTe thin film exposed to formaldehyde (a) 1 h of exposure, (b) 2 h of exposure, (c) 3 h of exposure and (d) 4 h of exposure.

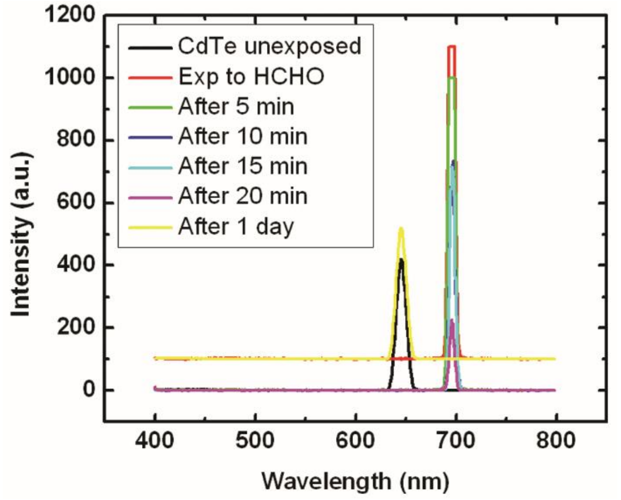

Fig. 13 — PL spectra of CdTe thin film exposed to formaldehyde and film observed for varying durations after exposure.

same intensity and wavelength. It can be concluded here that CdTe thin film is highly sensitive towards formaldehyde vapors and the film surface is recoverable after exposure to formaldehyde.

It can be seen from Fig. 13 that when CdTe thin film is exposed to formaldehyde for 5 min, the PL spectra shows a peak a sharp intense peak indicating the detection of formaldehyde. PL spectra recorded later after exposure from 5 min to 20 min, the intensity of peak reduces. PL spectra recorded the next day matches with the PL spectra of CdTe film unexposed thus confirming that the film surface can be regained after exposed to formaldehyde.

## 4 Conclusions

A good quality CdTe compound was grown by VDS method. The compound shows very sharp and well resolved peaks of CdTe. Some good quality stoichiometric thin films of CdTe were also prepared at different substrate temperatures and varying film thicknesses. Thin films deposited by thermal evaporation technique were found to have nano sized grains, uniform, continuous, poly crystalline in nature having cubic structure. An increase in the particle size is observed in AFM and SEM images when the substrate temperature is increased in CdTe thin films.

When CdTe thin films were exposed to vapors of benzene, toluene, methanol, ethanol and chloroform; we observe that the film surface has been damaged due to exposure of these organic compounds. Hence CdTe thin films cannot be used as a sensor for these organic compounds. A very high intensity peak as observed in PL study shows that these films can also be used as photo luminescent materials after detailed research.

CdTe thin films on exposure to vapors of formaldehyde and acetone, PL spectra and AFM show that the film surface is recoverable after exposure to these organic compounds. This shows that CdTe thin films can be used as sensors for formaldehyde and acetone.

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