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Effect of Hydrogenation and Annealing on ZnS/CdS/CdTe Thin Film for Solar Cell Application

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Abstract: In this paper, we used thermal evaporation method to deposit ZnS/CdS/CdTe triple layer thin film on a cleaned glass substrate under the pressure of 10-5 torr and carried out the effect of hydrogenation with different Hydrogen pressure, also see the effect of annealing. To study the change in an energy band gap due to hydrogenation and annealing, UV-VIS-NIR spectrophotometer has been used; there were three band gaps found, as 1.68, 2.0 and 3.90eV for CdTe, CdS and ZnS, respectively, and it is also observed that when thin films are hydrogenated and annealed together, then the band decreases. The XRD result of ZnS/CdS/CdTe thin film shows the peaks at a scattering angle (2θ) 23.78o, 28.72o, 39.34o, 46.41o and 55.50o corresponding to d-spacing 3.74, 3.08, 2.29, 1.96Å and 1.64Å, respectively, the cell parameters for CdTe, ZnS and CdS have evaluated as 6.48, 5.33 and 5.92Å, respectively. The Thermal electric power measurements indicate n-nature of thin film, and also with hydrogenation and annealing together the electron concentration increases resultant n-nature remained the same. The Seebeck coefficient for hydrogenation with different pressure at fresh, 80psi and 100psi have found 10, 20 and 40, respectively, and also Seebeck coefficient for hydrogenated annealing thin film are 10, 60 and 70, respectively. The purpose of this research is to see the change in the optical characteristic with hydrogenation and annealing so that it can be used to absorb more light from solar spectrum, to increase the efficiency of the solar cell.

Keywords: Hydrogenation, annealing, solar cell, thin film.

1 Introduction

In present, silicon-based solar cells can also be replaced by a thin film solar cell technology due to its low cost. In thin film technology, CdTe is the most popular and capable material [1]. The maximum theoretical efficiency of CdTe based solar cells is 28-30% [2], while in lab scale, its efficiency is approximately 20% and 16.5% in modules [3]. This major difference in theoretical and experiment occur because theoretical studies ignore optical, recombination, and the losses in space-charge region [4]. CdS can be used as the window layer n-type material for CdTe based solar cell, as it has a high band gap of 2.4eV, so the shorter wavelength photons can pass easily, resulting in the minimum absorption loss [5]. The efficiency of CdTe solar cells depends upon the energy band gap of window layer material (CdS). Increasing the band gap of CdS allows more photons to pass through it and reach at the absorber layer, while the lower band gap disallow photons to reach at the absorber layer, which reduces the solar cell performance. The annealing treatment is used to vary the band gap of the CdS window layer [6]. The thickness of CdS is also a very important part to increase the solar cell performance, as decreasing the thickness of CdS leads directly to increasing the solar cell efficiency because more photons reach absorber layer, but while reducing the thickness, it will increase the probability of diffusion of CdS into CdTe, but it is difficult to obtain a pin-hole free CdS layer [7]. This difficulty can be solved by adding a wide gap material layer on the CdS layer; only then, the thickness of the CdS layer can be reduced to a significant level. For this experimental works have done to make ZnS/CdS/CdTe solar cell [8]. The thickness of an absorber layer (CdTe) also plays an important role to improve the solar cell performance; enough thickness absorber layer collect approximate all photons, while thinner absorber layers collection becomes lower, which resultantly lower the solar cell efficiency.

In our work, we have studied the effect of hydrogenation



and annealing on optical property of ZnS/CdS/CdTe thin film which will be used in solar cell application; the wider band gap of ZnS allows more photons to reach at the absorber layer.

2 Experimental Details

All three layers of ZnS, CdS and CdTe were deposited using thermal evaporation method on a highly cleaned glass substrate under the pressure of 10-5Torr. Among the three materials purchased from Sigma Aldrich with 99.999% purity. For hydrogenation, a thin film has been placed in a hydrogen gas chamber at 80 psi and 100 psi, also, for annealing the hydrogenated thin films have been placed in a 500W halogen lamp for 1 and 2 minutes, respectively. To the band gap of materials, UV-VIS-NIR spectrophotometer is used, while seeing the effect of hydrogenation and annealing on energy band gap of material so that they can be in a good agreement with solar spectrum or solar cell performance. The X-Ray diffraction (XRD) have also done for the 2θ values $20^{\circ} < 2\theta < 80^{\circ}$; this result identifies the materials and their structure with dspacing, planes and cell parameters. The thermal electric power measurements have also been taken hydrogenated thin films; also for thermal annealed thin films for this treatment, a thin film is placed in a TEP box and heated from one corner of the glass slide measuring the current with a temperature difference and calculating the Seebeck coefficients, we also found that the nature of the thin film. which is n-type.

3 Results and Discussion

3.1 UV-VIS-NIR Result

The transmission spectra of ZnS/CdS/CdTe thin film has been observed by UV-VIS-NIR spectrophotometer with the wavelength shown in Figure1; this is done in a fresh one (at room temperature), at 80 psi hydrogen pressure with a one minute annealing and at 100 psi hydrogen pressure with a 2 minutes annealing in a 500W halogen lamp. The transmission spectra among three thin films shows that the transmission has increased with hydrogenation and annealing, also one can find that the transmission was varying with the wavelength; it's got lower values near 320, 620 and 740nm.

The absorption spectra of prepared hydrogenated and annealed thin films of ZnS/CdS/CdTe has been observed, using UV-VIS-NIR spectrometer with wavelength in the range of 300 to 800 nm. As shown in Figure 2. This Figure shows that the absorption has changed with the wavelength; it can easily be found that the absorption near the wavelength 320, 620 and 740 nm has compared to its near wavelength.

We have used a Tauc relation to calculate the energy band gap of the ZnS/CdS/CdTe thin film.

$$\alpha h \nu = A (h \nu - Eg) m....(1)$$

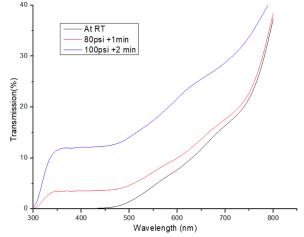


Fig. 1: Transmission spectra of ZnS/CdS/CdTe thin film.

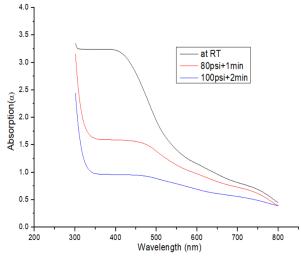


Fig. 2: Absorption spectra of ZnS/CdS/CdTe thin film.

Where 'A' is a constant, 'Eg' is the band gap of the semiconductor material and 'm' indicates the type of transition, the value of m= 1/2, 2, 3 and 3/2 for direct allowed, indirect allowed, indirect forbidden and direct forbidden transitions, respectively.

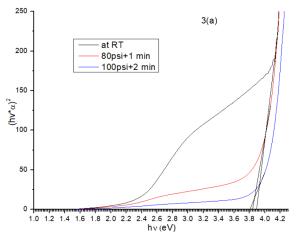


Fig.3:(a) plot for ZnS energy band gap calculation.

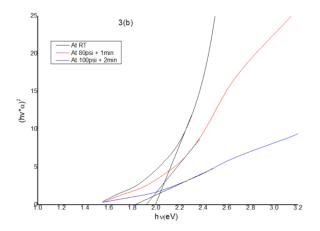


Fig. 3(b): plot for CdS energy band gap calculation.

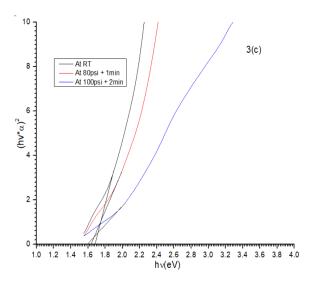


Fig. 3(c): plot for CdTe energy band gap calculation.

In our case (direct transition), the valve of 'm' is $(\frac{1}{2})$. To show the band gap clearly, we have used three different plots for different triple layer material as ZnS, CdS and CdTe as shows in Figure 3 (a, b and c), respectively. The band gap of Tri layer thin film observed with hydrogenation and different annealing time, the conclusion indicates that the band gap of ZnS for a fresh one (at room temperature), at 80 psi with a 1min. annealing and 100 psi with a 2 min annealing vary as 3.90, 3.84 and 3.80 eV, respectively; the band gap of CdS for a fresh one, at 80 psi with a 1 min. annealing and 100 psi with a 2 min. annealing vary as 2.0, 1.92 and 1.82eV, respectively; and the band gap of CdTe varies at 1.68, 1.64 and 1.60 eV, respectively; this is approximately the same band gap value for ZnS, CdS and CdTe that was also observed [9], in the following paper graded band film gap thin glass/FTO/ZnS/CdS/CdTe/Au has been deposited using electro deposition method. By increasing the annealing time and the hydrogen pressure (hydrogenation) the decrease in the band gap is also found by [10 and 11]. In the following paper the thin film of CdS has been deposited using the

spray pyrolysis method, and seen the effect of different annealing temperature as 300, 400 and 500^{0} C, they had done UV-VIS and found that the band gap of CdS vary in the range of 2.51 to 2.8eV.

The decreasing order in the band gap may be due to the hydrogenation and annealing effects; the numbers of defect states in the material are minimized, and it may be in transition from the amorphous to the crystalline state.

3.2 XRD Result

To study the crystal structure and identify the material, XRD was performed for the thin films. From the X-ray diffraction (XRD) pattern, we can calculate d-values by the diffraction peaks of the XRD spectrum using Bragg's relation.

$$2d\sin\theta = n\lambda$$

(Here, n = 1 in our case, $\lambda = 1.54060$ nm for Cu target).

To study the structural perfection of the interface region, the full-width at half maximum (FWHM) is considered. The Debye-Scherer formula is used to calculate the particle size.

$$D = \frac{0.94 \,\lambda}{\beta \cos \theta}$$

Where λ is a wavelength of X-ray, D is the denoted crystallite size and β is the full width half maxima (FWHM); it is in radians and θ is Bragg's angle here. The XRD pattern of ZnS/CdS/CdTe thin films is shown in Figure 4.

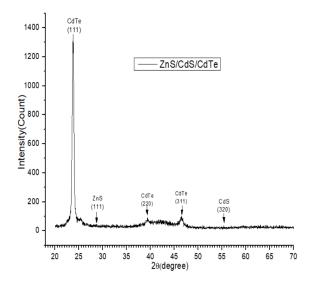


Fig. 4: XRD pattern of ZnS/CdS/CdTe thin films.

The above Figure 4 shows the XRD pattern of ZnS/CdS/CdTe thin film, we have observed peaks in XRD pattern at the scattering angle (2θ) 23.78°, 28.72°, 39.34°, 46.41° and 55.50° corresponding to d-spacing values 3.74, 3.08, 2.29, 1.96 and 1.64Å, respectively, we have also



observed that CdTe have the cubic structure with cell parameter $a=6.48\text{\AA}$ and we have found planes (111), (220) and (311) at angle (20) 23.78, 39.34° and 46.41° for CdTe, respectively, which is well matched with the data [12]. In the following paper, CdTe/CdS thin film have been deposited using chemical bath deposition (CBD), the XRD results shows (111) plane have been found for CdTe.

The other peak was found at the scattering angle (2θ) 28.72° for plane (111)with cell parameter $a=5.33\text{\AA}$ for ZnS. The Zinc Sulfide thin films were deposited on the glass substrate, by a chemical bath deposition [13], they have also found (111) plane orientation in XRD results. The last one peak have been seen for CdS plane (320) at the scattering angle (2θ) 55.50° with cell parameter a=5.92 Å, which is the same as observed [14]. From the same results of XRD with our data, one can easily identify the material and their structural characteristics, which is well matched with reported data.

3.3 Thermal Electric Power Results

For the thermal electric power measurement, we put thin films in TEP box and create the temperature difference on both corners of the thin films, by using a heater, now, currently noted with various temperatures, the plot between TEP versus the temperature gradient (ΔT) for the hydrogenated thin film as shown in Figure 5(a), by using the relation of Seebeck coefficient,

$$S = \frac{\Delta V}{\Delta T}$$

TEP measurement is done for the temperature range from 273 to 373K, and we evaluate the open circuit voltage corresponding to it. The polarity of thermally generated voltage was found negative; it had indicated the nature of the thin film is n type or the majority charge concentration of electron was present. According to plot, The TEP is decreasing continuously for the thin films, but with hydrogenated thin film at 80 psi and 100 psi the TEP decreases fastly. The Seebeck coefficient values for the thin film at room temperature (fresh), 80 psi and 100 psi have evaluated as 10, 20 and 40 µV/K, respectively. This is a well matched result with [15], in this paper, BiSbTe thin film have been prepared using the electro deposition method and they investigated that the Seebeck coefficients are increased with the increasing annealing time, also they found that the peak value of Seebeck coefficient was recognized at 350°C annealing.

It results in that with increasing annealing temperature, the thermoelectric property of the thin film had increases.

Now, the TEP measurement has also been done for the hydrogenated and annealed thin film of ZnS/CdS/CdTe, as shown in Figure 5(b). According to the Figure, we have found that the TEP is decreasing with the temperature gradient, and for annealed thin films, it is decreasing fastly, the Seebeck coefficient for these thin film have also been

calculated and it is found to be 10, 60 and 70 μ V/K for a fresh one (at room temperature), 80 psi with a 60 sec. annealing and 100 psi with a 120 sec. annealing, respectively. This is a well matched result with [16], they have found that with introducing hydrogen in Silicene, the Seebeck coefficient increases.

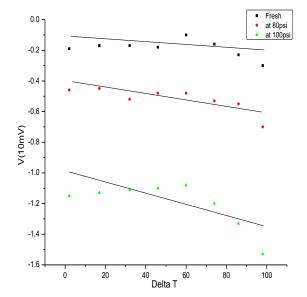


Fig. 5(a): Plot for Seebeck coefficient with different annealing times.

On comparing the above two results of annealing and hydrogenation effects, we have investigated that hydrogenation is the key process to increase the Seebeck coefficient or thermoelectric property of thin film. That results in increasing the free charge concentration in thin film that is required to improve the solar cell performance.

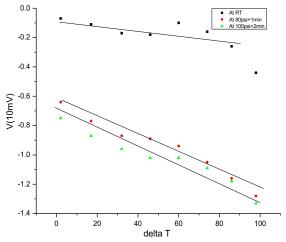


Fig. 5(b) Plot for Seebeck coefficient with different hydrogenated and annealing times.

We concluded that using annealing can change more in the Seebeck coefficient of thin films or free charge concentration of the material, which may be useful for increasing the property of the solar cell.



3.4 Scanning Electron Microscope Results

To see the surface morphology of the thin film ZnS/CdS/CdTe, we have used SEM techniques. The Figure 6(a) shows the SEM image at 10,000X, it can be seen that the surface is uniformly deposited and there is no pin hole found, while Figure 6(b) shows the SEM image at 50,000X, and it shows that the surface of the thin film is rough, small particles and grains could be seen easily, which is in good agreement with solar cell properties.

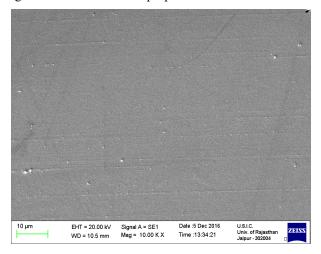


Fig. 6(a): SEM at 10,000X.

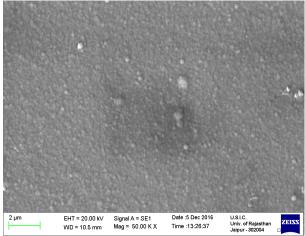


Fig. 6(b): SEM at 50,000X.

4 Conclusions

The UV-VIS-NIR result of hydrogenated thin film have shows that there were three band gaps found as 1.68, 2.0 and 3.90eV for CdTe, CdS and ZnS, respectively, also it is found that the band gap has decreased for the hydrogenated annealed thin film as fresh, 80 psi with a 1 minutes annealing and 100 psi with a 2 minutes annealing omit, it should be used to shift the absorption area in the solar spectrum to increase the solar cell efficiency. In the XRD results, peaks are found at the scattering angles (2θ) 23.78o,

28.72o, 39.34o, 46.41o and 55.50o. We also found planes (111), (220) and (311) for CdTe, plane (111) for ZnS and plane (320) for CdS. The TEP results identifies the nature of thin films as n type, therefore the majority of the charge carrier are electrons there, we also found that the Seebeck coefficient is increased with hydrogenation and annealing, which can be used to modify the material characteristics for the solar cell application.

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