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Research Article

THE INFLUENCE OF POST-ANNEALING CdS THIN FILMS GROWN ON ZnO SEED LAYER FOR CdTe SOLAR CELLS

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ABSTRACT

In this study, the effect of post-annealing temperature in CdS thin films grown on ZnO seed layer was investigated. CdS thin film and ZnO seed layer were coated by chemical bath deposition method and solution dropping technique, respectively. The structure of the post-annealed samples at 350°C and 400°C consisted of cubic CdS and $CdSO_3$ oxide phases. As a result of recrystallization at 450°C, both hexagonal CdS and cubic CdO phases were formed. While the absorption edge was observed at around 500 nm in all samples, the best transmittance was observed in the sample annealed at 400°C. PL spectra proved the existence of defect types such as deep emission, sulfur vacancy for all samples. Ellipsometer measurements showed that the highest refractive index was in the sample annealed at 400°C. Among the samples, it was concluded that the most suitable window structure for CdTe solar cell applications is CdS thin film post-annealed at 400°C.

Keywords: CdS, ZnO seed layer, CBD, post-annealing temperature

1. INTRODUCTION

In CdTe based solar cells, CdS thin films are conventionally used as n-type junction partners [1, 2]. CdS stands out with its surpassing features such as suitable band gap (~2.4 eV), high photoconductivity, low absorbance and high optical transmittance required for high performance photovoltaic devices [3, 4]. CdS can be grown by many methods such as vacuum evaporation [5, 6], spray pyrolysis [7, 8], close space sublimation [9, 10], RF sputtering [11, 12] and chemical bath deposition (CBD) [13, 14]. However, CdS layer in high efficient CdTe cells is usually grown by CBD method due to the possibility of recrystallization and alloying [15-17]. CBD method provides advantages such as repeatable and controlled process management, adjustable parameters (bath temperature, source concentration, etc.), simple and low cost production [18, 19]. However, problems such as low adhesion, non-uniformity, inhomogeneity may be encountered in the film growth process with CBD [20]. One of the ways to overcome these problems is to change the film growth parameters such as bath temperature, stoichiometry (cadmium/sulfur ratio), the amount of a complexing agent, etc. These changes in the film growth parameters in CBD method directly affect the reaction properties. In this sense, it was deduced that this parameters had a significant effect on the properties such as the crystal structure, grain structure, homogeneity, band gap, transmittance, carrier concentration and resistivity [21-27].

Although these adjustments in growth parameters seriously affect the properties of the films, there are still some difficulties with the desired film quality. In this context, growing CdS thin films onto a seed layer may be a solution to improve film properties. Due to poor quality of film growth, the seed layer plays especially an effective role in the improvement of low adhesion and nucleation [28]. Among the many materials used as seed layer, one of the most suitable for CdS thin films is ZnO. Growing CdS thin films on ZnO seed layer may provide a substructure to advance film properties. However, due to the amorphous nature of CdS deposited by CBD method, an extra processing is needed to improve the crystalline and morphological properties. In this direction, one of the most proper option is heat treatment. The annealing process leads to many effects such as increasing the crystal quality of the films, phase transformation, improving the grain structure, progressing of the optical and electrical properties [29-31].

Considering all aspects, it is thought that depositing CdS thin film on a seed layer followed by heat treatment is an effective process to develop the characteristics of CdS. In this sense, the effect of post-annealing on the structural and optical properties of CdS thin films coated on ZnO seed layer was investigated in this study. For this purpose, post-annealing temperatures ranging from 350°C to 450°C were used.

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2. MATERIAL AND METHOD

In order to search the effect of post-annealing temperature on CdS thin films grown on ZnO seed layer, the samples were coated on soda lime glass (SLG) substrates. Before coating ZnO seed layer, the SLG substrates were cleaned with acetone, isopropanol and de-ionized water in an ultrasonic bath. Then, ZnO seed layer was grown on the SLG substrates. The solution of ZnO seed layer was prepared using 5 mM zinc acetate dehydrate [$Zn(OOCCH_3)_2$] in absolute ethanol. 1 drop/cm^2 volume of the solution was dropped onto the substrates, and the surface was dried with N_2 gas after dwell time for 20 s. This operation was repeated eight times. After ZnO seeding, the prepared samples were annealed at 350°C for 30 min at air atmosphere [32]. CdS thin films with CBD method were grown using with a mixture of 15 mM $3CdSO_4.8H_2O$, 1.5 M thiourea and 28-30% ammonia hydroxide at a bath temperature of 80°C [33]. The thickness of CdS was set to 50-60 nm for a deposition time of 10 min. The samples were post-annealed for 20 minutes in air atmosphere at temperatures of 350°C, 400°C and 450°C. The prepared samples with post-annealing are schematically shown in Figure 1. In the whole text, labels were used to describe the samples. For example, label ZC-400 refers to the sample post-annealed at 400°C after the CdS thin film is grown upon ZnO seed layer.

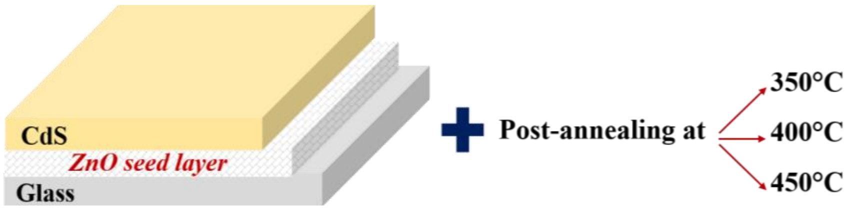

Figure 1. Schematic configuration of CdS samples grown on ZnO seed layer annealed at different temperatures

The crystallinity properties of the samples were analyzed with XRD spectra measured by Rigaku Smartlab diffractometer using CuK$_\alpha$ radiation. Transmittance curves were obtained using Dongwoo Optron UV-Vis spectrophotometer in the wavelength range of 300-1000 nm. Photoluminescence measurements at room temperature (RTPL) were performed with SpectraMax M5 at excitation wavelength of 280 nm. Refractive indexes was measured by J.A.Woollam spectroscopic ellipsometer.

3. RESULTS AND DISCUSSION

The XRD spectra of the samples post-annealed at 350°C, 400°C and 450°C are shown in Figure 2. As seen in Figure, there are overlapping and shouldering peaks in the diffraction patterns of the samples. To detect these peaks, the deconvolution process was applied to the spectrum of each sample. The peaks clarified by the deconvolution are also seen in the Figure. It was observed that the samples annealed at 350°C and 400°C had similar XRD spectra. According to the peak positions in the spectra, (111), (220) and (311) planes of CdS crystallizing in cubic structure were formed at 350°C and 400°C (Card No: 00-010-0454). In addition, $CdSO_3$ oxide phase was also formed in these samples (Card No: 01-078-1474). However, it was observed that the effect/intense of the oxide phase decreased at 400°C. Besides, the increase in post-annealing temperature from 350°C to 400°C led to an improvement from 8.8 nm to 9.8 nm in crystallite size calculated by Scherrer formula [34] based on the main peak of CdS.

In the deconvolution results of the sample post-annealed at 450°C, it was observed that the crystal structure of CdS phase transformed from cubic to hexagonal structure. In the spectrum, it was determined that (100), (002), (101), (110), (103) and (112) planes of hexagonal CdS were formed, respectively (Card No: 00-041-1049). In addition, it was detected that the (111), (200) and (220) planes of CdO phase crystallized in the cubic structure also exist in the crystalline structure of the sample (Card No: 00-005-0640).

Comparing of the XRD results showed that the samples at 350°C and 400°C had a similar crystal structure. However, as the post-annealing temperature increased to 450°C, the crystal structure of the sample underwent a radical change that CdS phase changed from cubic to hexagonal and that extra cubic CdO phase was formed. It was concluded that temperatures up to 400°C are not a high enough for recrystallization of the sample structure, but a temperature of 450°C is enough to drive the crystalline nature of the sample into a new formation. Besides, when the crystallization quality of the samples is examined, it can be said that ZnO seed layer improves the crystallization and allows more specific peaks to be revealed. Because it is known that CdS has nano-amorphic nature and may not cause a distinct change in crystallization even if heat treatment is applied at high temperatures. However, in our samples, the crystal structure of CdS was clearly determined with the support of the deconvolution process. This shows that the ZnO seed layer provides an infrastructure to grow higher quality films, in accordance with its purpose.

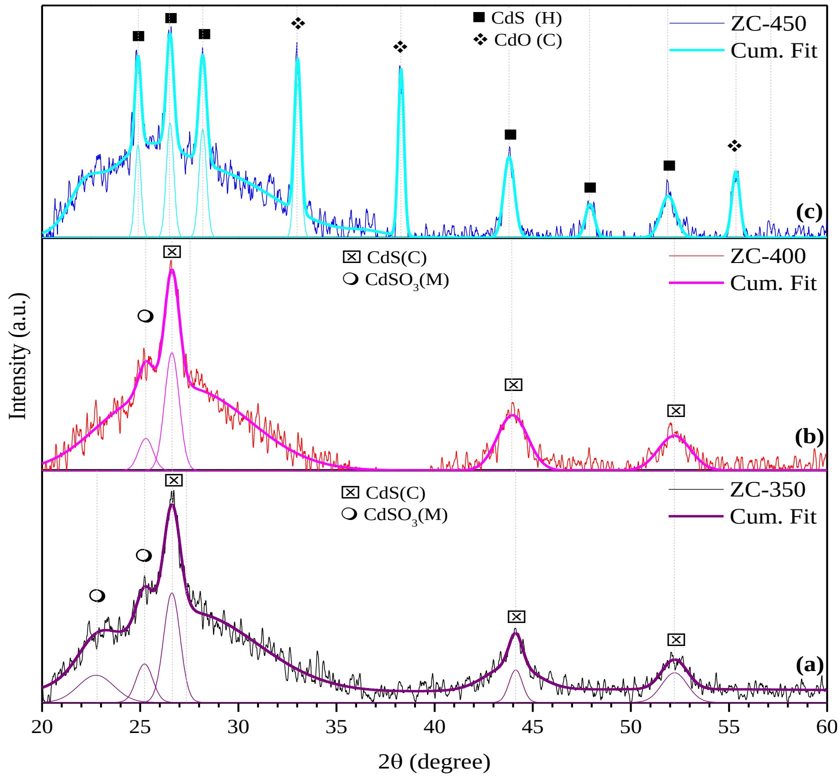

Figure 2. XRD spectra and corresponding deconvolution results of the samples post-annealed at **a)** 350°C, **b)** 400°C and **c)** 450°C (C, H and M in parentheses refer to cubic, hexagonal and monoclinic, respectively)

The transmittance curves of the samples between 300-1000 nm are shown in Figure 3. In the transmittance curves, it is seen that all samples have an absorption edge of around 500 nm, corresponding to CdS. In the wavelength region greater than 500 nm, the transmittance varied between 65% and 85% (at wavelength of 850 nm). Herein, it has the lowest transmittance to the sample post-annealed at 350°C. Increasing the annealing temperature to 400°C caused a 20% increase in the transmittance of the sample, resulting in transmittance of 85%. It can be said that this increment is due to the improvement in the crystallization at 400°C. However, the annealing temperature at 450°C led to a significant decrease in the transmittance. This reduction confirmed with the XRD results which showed that annealing at 450°C caused a serious change in the crystal structure of the sample.

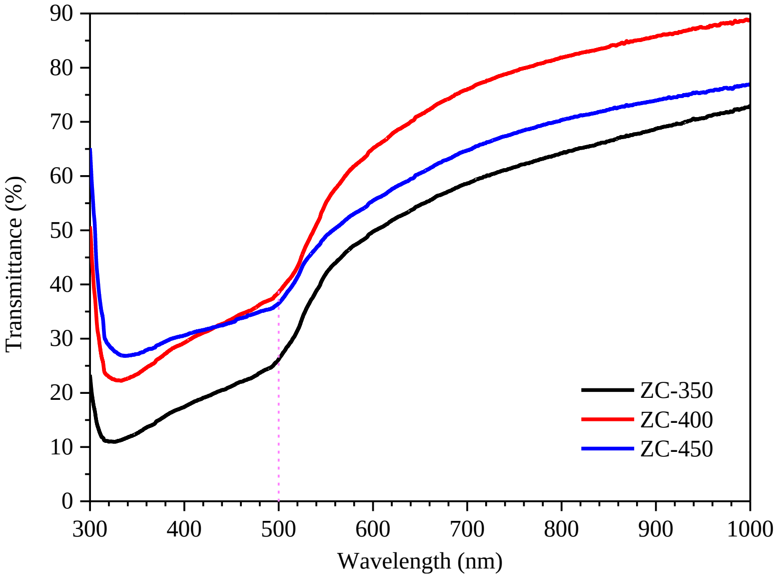

Figure 3. Transmittance curves of the samples post-annealed at 350°C, 400°C and 450°C

Room temperature photoluminescence (PL) spectra and corresponding deconvolution results of the samples post-annealed at 350°C, 400°C and 450°C are shown in Figure 4. When the figure is examined, it is seen that the samples have similar PL spectra. According to the deconvolution results, it was revealed that there were PL emission peaks around 360, 420, 443, 481-485, 530-535 (except 450°C) and 567 nm in all samples. The emission at 360 nm is attributed to transitions from deep levels to shallow levels, while the peak at 420 nm corresponds to the band edge emission [35, 36]. The emission at 443 nm is related to band-edge emission from radiative recombination of excitons [37], while the range of 481-485 nm is associated with host CdS [38]. The peaks around 530-535 nm and 567 nm are connected with vacancy sulphur defects (V_S) [39] and the transition between the interstitial cadmium (I_{Cd}) donor level and the acceptor level [40], respectively.

Unlike the samples annealed at 350°C and 400°C, a dominant CdO phase was formed at 450°C, according to XRD results. Therefore, transitions to CdO phase are also likely in PL spectrum at 450°C. In this context, it can be said that the peak at 485 nm is due to the transition between the conduction band and valence band of CdO. Also, the transition at 530 nm can occur with near band-gap radiative combination due to the oxygen vacancy of CdO material [41].

In the PL results, while the peaks corresponding to CdS were found in the samples annealed at 350°C and 400°C, the presence of recessive $CdSO_3$ phase was not encountered. However, the sample annealed at 450°C exhibited the emission peaks indicating the presence of the dominant CdO phase as well as CdS. In this context, it was concluded that the crystal quality and phase structure of the samples play an important role in PL spectrum.

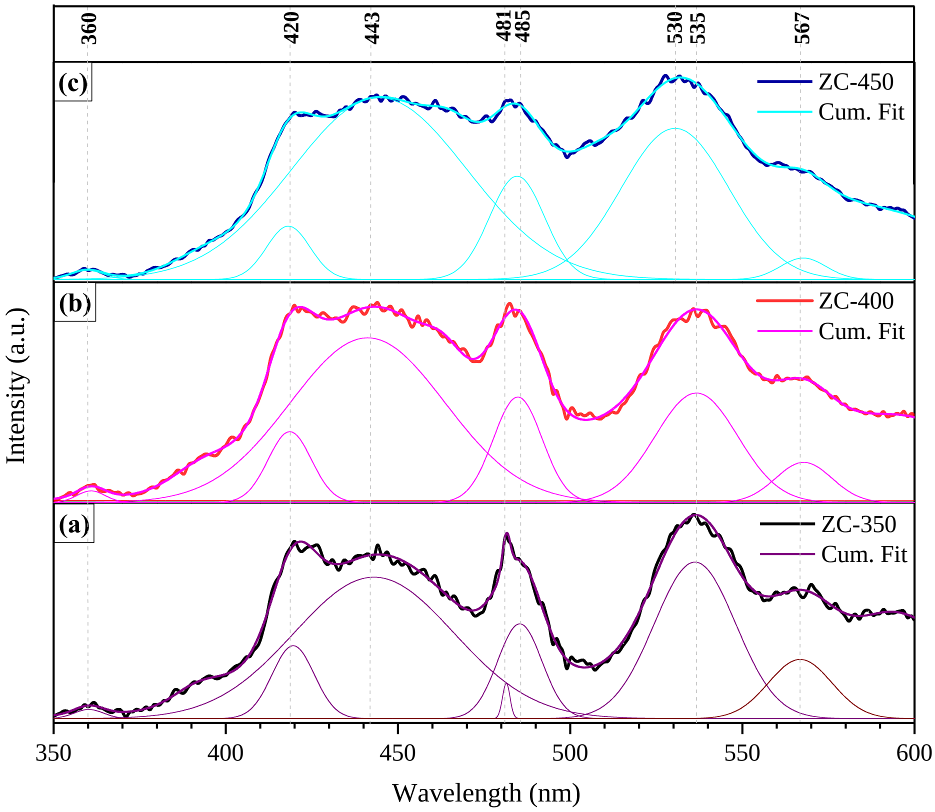

Figure 4. Photoluminescence spectra and corresponding deconvolution results of the samples post-annealed at 350°C, 400°C and 450°C

Refractive index curves of the samples obtained by ellipsometer measurements are shown in Figure 5. In the figure, the refractive index of all samples reached its maximum value around 520 nm, corresponding to the band gap of CdS. After 520 nm wavelength, the refractive index also decreased in response to increasing wavelength. As the annealing temperature increased from 350°C to 400°C, the refractive index also enhanced from 1.56 to 2.14 (at 520 nm). However, it decreased to 1.60 at the temperature of 450°C. It was thought that this change in the refractive indices was due to the transformation in the crystallization and phase structure, as seen in the XRD results. In general, it is seen that the refractive index values of the samples are low compared to the literature [42, 43]. It can be said that this situation is caused by ZnO seed layer which may act as an extinction layer.

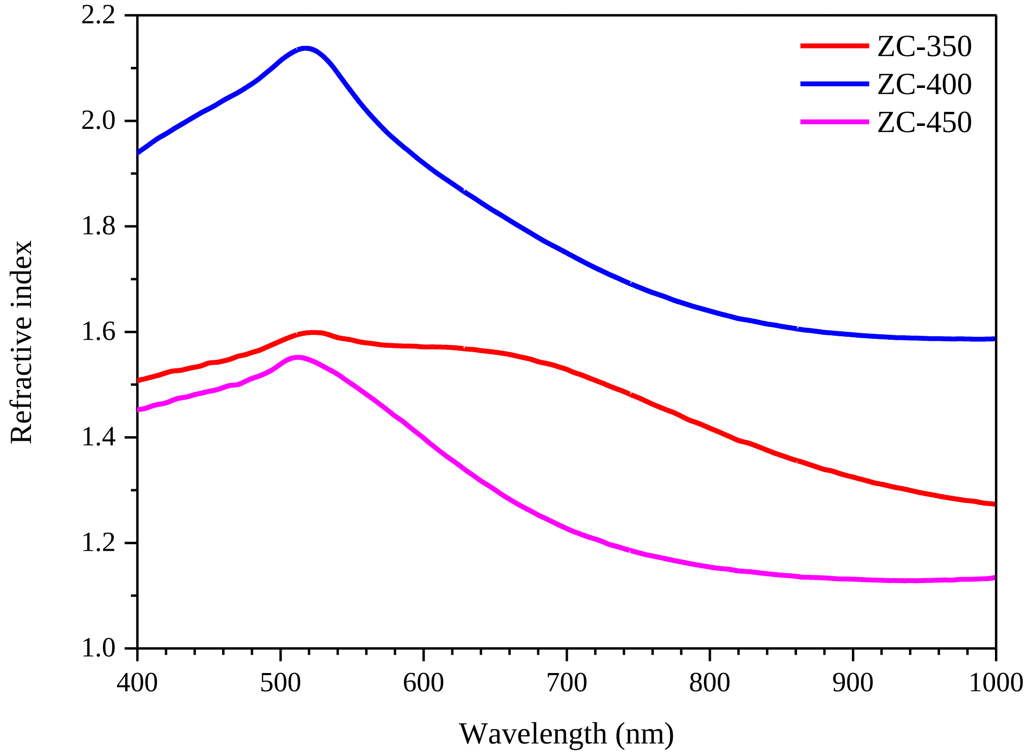

Figure 5. Refractive index curves of the samples post-annealed at 350°C, 400°C and 450°C

4. CONCLUSION

In this study, the effect of annealing temperature on CdS thin films grown on ZnO seed layer was investigated. CdS thin films and ZnO seed layer were coated by CBD method and wet processing, respectively. The samples were post-annealed at 350°C, 400°C and 450°C after film growth. XRD results showed that samples annealed at 350°C and 400°C had similar spectrum with cubic CdS and $CdSO_3$ oxide phases. When the annealing temperature reached 450°C, the crystal structure of the sample was completely changed. Accordingly, cubic CdS transformed into hexagonal structure and recessive $CdSO_3$ phase became dominant cubic CdO structure at 450°C. Transmittance curves showed that all samples had an absorption site of around 500 nm. Also, transmittance was improved when annealing temperature was increased from 350°C to 400°C. However, it was decreased at 450°C due to the transformation in the crystalline structure. PL spectra demonstrated that all samples annealed at different temperatures had a defect structure such as deep level and band edge emissions, host CdS, etc. In addition, PL peaks indicating the presence of CdO in the sample at 450°C were also observed in the spectrum. Ellipsometric measurements showed that the diffraction indices peak at 520 nm with the highest refractive index at 400°C.

Briefly, use of ZnO seed layer to improve the structural and optical properties of conventional CdS can provide a resource for improving device performance in CdTe solar cell applications. In the investigation of the annealing temperatures, it was concluded that post-annealing at 400°C would be more suitable for cell performance, considering the cubic nature of CdTe.

SIMILARITY RATE: 15%

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