Fabrication of high efficiency sputtered CdS:O/CdTe thin film solar cells from window/absorber layer growth optimization in magnetron sputtering

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\textbf{A R T I C L E   I N F O}

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XPS
PL
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\textbf{A B S T R A C T}

In this study, CdTe (up to 2.0 \textmu m thick) and oxygenated CdS (CdS:O, up to 100 nm thick) films were deposited by magnetron sputtering and optimum conditions of film growth were investigated for CdS:O/CdTe solar cells. Favourable TeO\textsubscript{2} has been confirmed in XRD after the CdCl\textsubscript{2} heat treatment of the CdTe films. Moreover, improved structural, optical and electrical properties are observed in the CdCl\textsubscript{2} heat treated films. A detailed quantitative study has also been executed using XPS that finds sulfide, sulfate and an intermediate oxide as a function of oxygen content. In many cases, CdS contribution remains predominant, however, the CdSO\textsubscript{x} contribution increases with the increase of oxygen’s partial pressure and decrease of growth rate. The complete solar cell device was fabricated of various CdTe thin films with different growth rates in sputtering. A highly resistive transparent (HRT) buffer layer ZnO:Sn was placed in between the FTO and CdS:O to avoid the forward leakage problem and screen printed C:Cu/Ag is used as the back contact for low cost fabrication. The J–V characteristics and external quantum efficiency (EQE) were measured for the solar cells under the illumination of AM 1.5G and the highest efficiency of 10.3\% was achieved for the optimized CdTe growth rate of 5.4 \textbar/\textbar/s, while CdS:O growth rate was 0.25 \textbar/\textbar/s.

1. Introduction

CdTe is the most promising and leading material among all the thin film solar cells’ absorber materials. The conversion efficiency as well as the commercial implication of CdTe photovoltaic (PV) technology have been growing rapidly over the past decade. A multi-giga-watt/year production has already been achieved by CdTe thin film photovoltaic manufacturers attributed to achieved high efficiency and lower fabrication cost. Cadmium Telluride (CdTe), owing to its direct optical bandgap (E\textsubscript{g} = 1.5 eV) and higher absorption coefficient of around 5 \times 10\textsuperscript{5} cm\textsuperscript{-1}, has already been recognized as the most promising compound semiconductor for solar PV application [1]. CdTe thin film solar cell efficiency has already reached to 22.1\% in laboratory [2] and 17.5\% in module scale [3]. However, to be a sustainable photovoltaic material, the cost should be reduced further possibly through the reduction of material usage, cell processing and balance of system costs. Therefore, reducing the thickness (\textless 2 \textmu m) of CdTe absorber layer to its theoretical limit of optical absorption without compromising the higher conversion efficiency is highly desirable. Needless to mention that among the other cost related parameters, a large portion of installed solar panel cost is directly related to the material usage [4]. However, the ultra-thin layer, i.e. thickness near to theoretical limit of solar spectrum absorption, provokes several problems like pinhole, shorting the front and back contact pinching through the window layer etc. This local shunting surely reduces the performance of the solar cell and increases the deep penetration loss. In the case of ultra-thin CdTe absorber layer, the cell performance is also affected by full or partial depletion of the layer and/or by interference between the p-n and/or contact junctions. Even though, the efficiency of CdTe-based solar cells is increasing rapidly, yet the conversion efficiency for a specific deposition technique, structural, optical and electrical properties are an open-ended problem for the ultra-thin CdTe solar cells. Any deposition process (e.g. sputtering) and post-deposition parameters such as growth rate and CdCl\textsubscript{2} wet-treatment are to be extensively investigated to get optimized ultra-thin CdTe layered solar cells.

A number of techniques were employed by the researchers...
well-known that the CdTe properties are also influenced by the growth rate. Improving the quality of the ultra-thin CdTe films has been proposed; however, too thin CdS reduces the open circuit voltage (Voc) and fill factor (FF) via pinholes as created by missing deposition and/or 100% diffusion of CdS to CdTe [12]. The minimum CdS thickness can be used for optimum cell efficiency via the addition of a high resistive transparent (HRT) layer [13] underneath of the CdS window layer. This configuration has been reported using SnO2 HRT layer [14]. However, the solar cells showed poor performance and need to be optimized in terms of current collection and other device parameters for higher efficiency. A higher bandgap window layer (Cd, Zn)S has also been approached and cell suffered from the low Voc and phase segregation issues as reported in literatures [15,16].

Another very different approach is luminescence downshifting using a polymer dye on the front surface of the cell [17]. The dye converts high energy photon to low energy which can pass through CdS; however, this process has only improved blue response by 16% [18]. Also, this process increases the cost of cell or module and it has stability issue of the polymer film. Therefore, the increase of transmission and reduced diffusion are considered to be the best way to improve efficiency in CdTe based solar cells. Reactively sputtered CdS in the presence of oxygen may have the potential to meet the above-required properties. Wu et al. [19] first prepared this material, named oxygenated cadmium sulfide (CdS:O) and reported structural, electrical and electrical properties. Later on, CdS:O film has been prepared by employing CSS followed by the post-deposition thermal annealing in oxygen ambient [20,21]. The presence of oxygen into the CdS:O films reduce film crystallinity, increase bandgap, reduce inter-diffusion and lattice mismatch at the junction region [19]. Many groups have been fabricating CdTe based solar cells, which have somehow similar configurations. However, in this study, the complete solar cell has also been fabricated with the novel structure of ‘glass/FTO/ZnO:Sn/CdS:O/CdTe/Cd/Cu/Ag’, where the back contact of the cell has been done by screen printing technique for its low cost potential, but it requires rigorous optimization.

2. Experimental procedure

At first, both CdTe and CdS:O films were separately deposited on top of bare soda lime glass substrates for characterization purposes and then optimized films were stacked for complete solar cell fabrication. CdTe thin films of about 2.0 µm were deposited on top of the soda lime glass substrate by RF sputtering at different growth rate ranging from 1.8 Å/s to 5.4 Å/s by controlling RF power from 1.0 W/cm² to 3.0 W/cm². The growth rates of the films were observed during the deposition by the thickness monitoring system (FTM-2000, TORR International, Inc.) embedded to the sputtering system. Table 1 shows the growth parameters including ambient pressure and temperature during the deposition. The glass substrates used in this study were cleaned by the several sequential steps in the ultra-sonication tube using acetone, ethanol and deionized water as the clean solution. The duration of each cleaning step was 10 min and finally samples were dried by dry N₂.

At an optimized RF power of 2.0 W/cm², CdS:O thin films of thickness around 100 nm were deposited on bare microscopic glass substrate at room temperature. The growth rate of the films was varied from 0.15 Å/s to 0.45 Å/s. The O2 partial pressure was varied from 11 mPa to 24 mPa during the sputtering by changing the pressure of argon:oxygen (99:1) gas mixture inserted to the chamber. It has been found that the deposition rate inversely changes with the increase of ambient pressure as expected. Therefore, to maintain the required film thickness, the deposition time was increased suitably with the increase of ambient pressure.

The structural properties and surface morphology were investigated using X-ray diffraction (XRD) spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM). XRD patterns were taken in the 2θ ranging from 20° to 70° using Cu Kα radiation wavelength of 1.5408 Å using “BRUKER aXs-D8 Advance Cu-Kα” diffractometer. The average crystalline size (D), microstrain (ε), and dislocation density (δ) have been determined by using the formula, D = 0.89 λ / β Cosθ [22], ε = β / 4tanθ [23] and δ = 1 / D² [24], respectively, where, θ is the Bragg’s or diffraction angle of the x-rays, β is the full-width half maximum (FWHM) of the reflection peak that has the same maximum intensity in the diffraction pattern, λ is the

| Table 1 |
|-------------------|-------------------|-------------------|
| **CdTe (300 °C)** | **CdS:O (RT)**    |
| Dep. power (W/cm²) | Flow rate (Ar) | Ambient pressure | Growth rate (Å/s) | Dep. power (W/cm²) | Flow rate (Ar/O = 99:1) | Oxygen partial pressure (mT) | Growth rate (Å/s) |
| 1.0, 8 sccm       | 1.8             | 2.0, 2 sccm      | 0.08             | 0.46             |
| 1.5, 2.5          | 2.5             | 4 sccm           | 0.12             | 0.32             |
| 2.0, 3.6          | 3.6             | 8 sccm           | 0.15             | 0.25             |
| 2.5, 4.6          | 4.6             | 12 sccm          | 0.18             | 0.15             |

Wu et al.[19] fabricated CdTe-based solar cells with CdS:O thin films. The CdTe thin films were deposited on glass substrates by RF sputtering at different growth rate ranging from 1.8 Å/s to 5.4 Å/s by controlling RF power from 1.0 W/cm² to 3.0 W/cm². The growth rates of the films were observed during the deposition by the thickness monitoring system (FTM-2000, TORR International, Inc.) embedded to the sputtering system. Table 1 shows the growth parameters including ambient pressure and temperature during the deposition. The glass substrates used in this study were cleaned by the several sequential steps in the ultra-sonication tube using acetone, ethanol and deionized water as the clean solution. The duration of each cleaning step was 10 min and finally samples were dried by dry N₂. As-deposited CdTe thin films have undergone the CdCl₂ heat treatment. A schematic diagram of the CdCl₂ process employed in this study is shown in Fig. 1. The samples were immersed in cadmium chloride solution of 0.3 M for 10 s. After the dipping process, they were dried naturally for 10 min and then, heated in an evacuated furnace of N₂/O₂ ambient for 15 min at 66.66 Pa pressure and at a temperature of 390 °C. After the completion of the heat treatment, the samples were washed in warm water for several times.

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wavelength of x-rays (0.15406 nm). AFM and SEM analyses of the samples were carried out using “INTERA PRIMA, NT-MDT” and “LEO 1450 Vp”, respectively. The surface topography, roughness and grain size and grain growth are observed from the AFM and SEM images. The carrier density, mobility, and Hall coefficients are measured by the Hall Effect measurement tool “ECOPIA 3000”. The optical properties are determined by the UV–vis spectrometry using “Perkin Elmer Instruments Lambda35”. Also, photoluminescence (PL) measurements of CdS:O films were carried out at room temperature with an “FLSP920 Edinburgh” spectrophotometer using the exciting light wavelength of 458 nm. The films surface chemical states were analysed by high-resolution, X-ray photoelectron spectroscopy (XPS). XPS measurements were performed on a “KRATOS/SHIMADZU AXIS ULTRA DLD” instrument. All XPS spectra were calibrated using the carbon C 1s peak (284.80 eV).

The complete solar cells were primarily fabricated on top of the commercially available fluorine-doped tin oxide (FTO) coated glass substrates with ZnO:Sn as a high resistive transparent (HRT) buffer layer, where Cu-doped carbon (C) and Ag were used as back contact. The entire back contact layers C:Cu/Ag were formed by the screen printing technique on top of CdCl₂ treated “Glass/FTO/ZnO:Sn/CdS:O/CdTe” stacks. At first, C:Cu layer was printed and dried at 120°C for 30 min in open air. After that, the complete stacks were annealed at 260°C in a vacuum furnace at 66.66 Pa pressure of N₂ for 15 min. During the vacuum annealing, Cu was facilitated to diffuse inside the CdTe and was expected to form a very thin CuₓTe layer on the CdTe surface. Finally, devices were completed by printing Ag as a secondary metal contact which was dried at 120°C for 30 min in open air. To the best of our investigation on similar works, it is found to be the first time reporting on sputtered CdS:O/CdTe solar cell with ZnO:Sn HRT layer and screen printed C:Cu/Ag back contact. The performance of the cells with an area of 0.25 cm² were evaluated under the illumination of AM 1.5G using “Gratings Inc. Solar Cell Tester: IV & power management system”. The external quantum efficiency (EQE) spectra of the cells were measured at room temperature using spectral sensitivity measuring equipment with an Xe lamp and monochromator using a CEP-2000 integrated system by Bunko-keiki Co. (Information Device Science Lab, Nara Institute of science and Technology, Japan), which irradiated light at 100 mW cm⁻² (AM 1.5G). The system was calibrated by a Si reference cell (S-1337BK) and the QE curve was taken in the range of 300–1000 nm with an interval of 20 nm. The effective irradiated area of each cell was kept as 0.25 cm² by using a light-tight metal mask for all samples.
Fig. 3. Structural properties of as-deposited and CdCl₂ treated CdTe thin films as a function of growth rate, (a) for the variation of texture coefficient (TC(111) – TC(220)), (b) W-H plot, (c) for the mean crystalline sizes with respect to the (111) plane and (d) for the dislocation density (solid lines) and strains (dotted lines).

3. Results and discussion

3.1. Analysis of CdTe thin films

The structural properties including material phases, crystallinity and the size of crystallites of the deposited CdTe films were investigated by the XRD as shown in Fig. 2. However, the terms texture coefficients, standard deviation, dislocation densities, and strains are extrapolated from the XRD spectra for exploring the growth mechanism of the CdTe films as shown in Fig. 3. Fig. 2(a) shows that the intensities of the (220), (311), and (400) peaks are very small compared to the (111) peak for the as-deposited films indicating that the crystallization was dominated along the (111) plane. Besides, the crystal orientation along the (111) increased with the increase of growth rate, perhaps due to the nucleation rate and/or due to the diffusion velocity of CdTe atoms that are enhanced by the growth rate of the films. After the CdCl₂ heat treatment, the (111) peak intensity is observed to decrease, and peaks belonging to other crystalline planes appeared to increase, which indicate that the CdCl₂ treatment enhanced the recrystallization process of the sputtered CdTe thin films. As an effect of recrystallization, the film deposited in between the rates of 1.8 Å/s to 4.6 Å/s showed random orientation. However, the treated film that was deposited at the highest growth rate of 5.4 Å/s has again found preferential orientation along (111) cubic plane. This implies that the grains of the films deposited at higher growth rate recrystallize promptly towards the (111) cubic plane during the CdCl₂ treatment than the film of lower growth rate. The deconvolution of the peaks (220) and (311) showed additional satellite peaks as seen in the inset of Fig. 2(b). The peak at 39.35° belongs to (201) crystal orientation of TeO₂ (JCPDS No. 76-0679) and the peak at 46.45° belongs to (003) crystal orientation of Te (JCPDS No. 36-1452) [25,26]. However, there is another significant TeO₂ peak that belongs to (102) crystal plane in the film grown at the rate of 3.6 Å/s. Oxygen from the ambient during the CdCl₂ treatment may have reacted individually with the elemental Cd and Te and thus CdO and TeO₂ may have developed. However, CdO is dissolved in the solution during the post-treatment cleaning process and part of Te and/or TeO₂ has remained at the surface of CdTe thin film. As a result, no CdO peak is observed and Te-rich surface is developed. Moreover, slightly higher amount of Te is also confirmed from the EDX analysis, which will be described later in the next section. Similar results have also been reported by Chun et al. [26] for wet chemical CdCl₂ heat treatment of CSS grown CdTe films.

Both grain growth and recrystallization during the CdCl₂ treatment are quantitatively investigated by the texture coefficient (TC) as shown in Fig. 3(a). Texture coefficient (TC) along the preferential orientation (hkl) has been calculated as reported in reference [27]. The increasing trends of [TC (111) – TC (220)] values for every as-deposited films indicate that (111) plane orientation is increasing in the films with respect to the growth rate. On the other hand, the values of [TC (111) – TC (220)] are less than 1 of the CdCl₂ treated films, except the film growth at 5.4 Å/s. This suggests that the films are randomly oriented, which may be due to the reorientation rate variation for the films grown at slower rate than the films deposited at 5.4 Å/s. Moreover, the new-born peaks such as (400) at 56.64° and (331) at 62.39° indicate that the CdCl₂ heat treatment enhances the polycrystalline nature of CdTe thin films. As the crystallographic rearrangements of CdTe thin films are related to the CdCl₂ sintering flux, textures, and strains in the film and annealing temperature, the deposited films show a different behaviour in this study.

The lattice parameters ‘a’ for the as-deposited and treated films are determined from the Brag’s law and the Vegard’s law [23]. The accurate values of the lattice parameter (a) for the cubic phase were calculated and are shown in Fig. 2. It has been observed that the lattice parameters ‘a’ of the CdCl₂ treated films are smaller than that of as-deposited films. This decrease in the lattice parameter demonstrates that the films are subjected to a tensile strain in the plane parallel to the substrate surface due to the internal stress on the crystallites and/or due to the lattice mismatch and differences in thermal expansion coefficients [28]. The changes in the lattice parameters are in well agreement with the Williamson–Hall (W–H) plot as shown in Fig. 3(b). The W–H analysis is well known as an effective technique for the determination of strain evolution and its magnitude from the peak broadening characteristics [21]. The nature of strain can also be predicted from W-H plot, where, a negative slope indicates a compressive strain, and a positive slope is the signature of tensile strain. From this study, it is revealed that the strain and its nature in the film are found to have a direct correlation with the growth rate. However, the lattice parameter could also be affected by the recrystallization process and change in the Cd/Te compositional ratio as discussed later.

The polycrystalline CdTe thin films of random orientation suggested that a large number of grains with various relative positions and orientations cause variations in the phase difference between the wave scattered by one grain and the others that originate lattice misfit. Merely, this phenomenon is defined by microstrain, which in turn, depends upon the growing conditions and post-deposition process of the films. The calculated micro-strain for the films is shown in Fig. 3(d), as the lowest micro-strain is found for the film of growth rate at 4.6 Å/s, indicating the films’ perfections. Also, Fig. 3(c) and (d) show the variation of crystallite size and dislocation density with respect to the growth rate. As the dislocation densities and strains are reduced in the films deposited at higher growth rate, the structural defects of the deposited CdTe thin films have reduced upon improving the stoichiometry of the films. Consequently, the crystallite sizes have increased. Overall results have demonstrated the significant effect of the films’ growth rate and the CdCl₂ solution treatment. The variation in crystallite size, dislocation density, and strain with respect to the growth rate indicates that the film grown at 4.6 Å/s is found to be the best quality film in this study. The film has low dislocation density, bigger crystallite size, and the lowest strain with nearly random orientation.

The SEM surface morphology and AFM topography image of as-deposited and corresponding CdCl₂ treated films for the growth rate at 4.6 Å/s are shown in Fig. 4. The estimated surface roughness of all the films is shown in Table 2. Before the CdCl₂ heat treatment, the grain size of the films was smaller as can be found in Fig. 4 and roughness is mostly in single digit nanometer order, whereas grain size has increased significantly as well as the roughness to an order of magnitude for the samples after CdCl₂ heat treatment. As mentioned earlier, there is a probable cadmium etching from the surface of the films during the cleaning process as one of the steps of CdCl₂ heat treatment. Cadmium-
etching has resulted in Te-rich CdTe surface that is also confirmed by the EDX (Cd/Te in Table 2) and XRD.

SEM image of the as-deposited film shows an array of smaller grains, which are diffused during the CdCl₂ treatment and eventually resulted in enlarged grain size. Fig. 4(e) and (f) shows the grain size of all the films corresponding to the growth rate. The average grain sizes were estimated by ‘image-J’ software. A clear evidence of the effect of growth rate and subsequent CdCl₂ heat treatment is observed from the figures.

The biggest grain among the as-deposited films is found for the films of the growth rate of 3.6 Å/s. Maybe the diffusion and nucleation during the deposition is the highest at this growth rate that helps to form bigger grains. The biggest grain size (up to 1.7 µm) is found for the film grown at the rate of 4.6 Å/s among the CdCl₂ heat treated films. The small grains are diffused during the heat treatment and increase the grain size. Nevertheless, the increase of the grain size and/or diffusion velocity is depending on the strain and dislocation densities of the films.

Optical bandgap (Eg) of the CdTe thin films were calculated using the well-known Tauc plot [29] as shown in Fig. 5(a) and (b). It is found that the CdCl₂ treated films are having lower bandgap than as-deposited films. The decrease of the band gap can be attributed to the increase of roughness of the films as confirmed from AFM image analysis (Table 2), which leads to increase the photon scattering [30]. Moreover, both Te and carrier concentrations vary as an effect of the CdCl₂ treatment, which lead to increase the width of the localized states available in the conduction band of the films and reduce the bandgap. This phenomenon affects the absorption coefficient (α) near the band edge (Urbach tail) for which an exponential dependence on photon energy for many materials is observed [31]. In order to illustrate this dependence, the ln (α) vs. (hv) has been plotted as shown in the inset of the Fig. 5. The exponential increase of the absorption coefficient (α) in the range of the absorption edge can be explained from the transitions between the tails of density-of-states in the conduction band and the valence band, the shape and size of these tails. According to the Urbach-Martienssen model [32,33], the main parameter represented by Urbach energy (Eₚ) determines the photon capture efficiency of a semiconductor layer.

The Eₚ values for the films have been calculated from the slope of the band edge to be 1.5 eV using relationship, Eₚ = (Δln(α) / Δ(hv))⁻¹. The higher values of Eₚ in the deposited CdTe films indicate the higher phonon state disorder and/or higher doping concentrations in the films. In contrast, the highest value of Eₚ is found for the film deposited at growth rate of 4.6 Å/s and secured high carrier concentration. Mott and Davis [34] noted that the binary semiconductor compounds present a particular optical absorption edge profile while they are doped by a particular ion, where the fundamental edge is mainly determined by valence band maximum and conduction band minimum levels. In CdTe material, the Eₚ values are correlated with the Cd/Te ratio, which could

Table 2
Surface roughness, Urbach energy, carrier concentration and Hall mobility of CdTe thin films as a function of growth rate prepared by sputtering technique ((a) is for as-grown and (b) is for CdCl₂ treated films).

<table>
<thead>
<tr>
<th>Growth rate (Å/s)</th>
<th>Roughness Rrms (nm)</th>
<th>Urbach energy Eₚ [meV]</th>
<th>Carrier concentration [× 10¹⁵ cm⁻³]</th>
<th>Hall mobility [cm² V⁻¹ s⁻¹]</th>
<th>Elemental ratios (Cd/Te)</th>
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be understood from fine scale defect formation mechanisms in CdTe crystals during deposition and the melt growth dynamics that take place during CdCl₂ heat treatment [35]. It is assumed that the nature of the structural disorder in as-deposited films is dominated by intrinsic defects such as dislocation and/or vacancies, while in CdCl₂ treated films it is dominated by external factors, such as, deviation from stoichiometry, ion implementation and doping, etc. Also the amorphous glass substrate may influence the Eu of the CdTe films.

The carrier density of the films are in the order of 10¹³–10¹⁴ cm⁻³ as shown in Table 2, which shows an increasing trend with the increase of growth rate. Besides, the carrier densities further increased several times with the CdCl₂ treatment. As the surface becomes Te-rich due to the CdCl₂ treatment, the p-type conductivities as well as carrier concentration of the films increased. The results are quite similar to the previous report on Te-rich CdTe thin films deposited by the CSS technique [36]. However, the Hall mobility of the CdCl₂ treated films is found lower than the as-deposited films, maybe due to the higher surface roughness of CdCl₂ treated films. The mobility values changed anomalously, which fails to be correlated with the growth rate. It may be related to the grains, dislocation, and strain. More study is needed to reveal the exact factors. In contrast, the resistivity found in this study is quite similar to those reported by other groups (10⁴–10⁸ Ω·cm) [37]. The variations of films’ properties are indicating the significant effect of the growth rate as well as the CdCl₂ treatment.

3.2. Analysis of CdS:O thin films

The surface elements and chemical states of the deposited CdS:O films were investigated by high-resolution XPS analysis. Fig. 6(a) shows the XPS multiplex spectra of CdS:O film deposited at a growth rate of 0.25 Å/s. XPS measurement indicates that the films are of a composite structure having CdSO₄, CdS, and CdO. The compositional ratio are shown in Table 3 as found from the XPS analysis. As the XPS multiplex spectra of CdS:O film contain complex forms, they are assigned to the corresponding species through a deconvolution fitting procedure. As shown, Cd 3d peaks of the film located at around 405 eV and 411.8 eV are symmetric, which are assigned to the Cd 3d₅/₂ and 3d₃/₂ states [38]. As can be seen for S 2p peak in Fig. 6(a)(ii), deconvolution peaks

![Graph](image-url)
are corresponding to the binding energies of 161.6 eV, 162.5 eV and 163.2 eV that are assigned to CdS and 168.8 eV is assigned to CdSO$_4$ complexes [39]. It appears that S atoms are individually combined with O and Cd atoms, which form SO$_4$ complex and CdS nano-particles during the reactive sputtering. The O 1s spectrum envelopes were fitted by three peaks; where the first peak located at the lower binding energy of 530.9 eV attributed to (O)$_2$ and the second peak located at the binding energy of 532.5 eV (for 0.1216 mPa pressure), and in principle could be related to the bond with (Cd)$_2$O in the form of CdO [40]. Ferekides et al. also reported the similar phenomena for CSS grown CdS thin films deposited in O ambient. They proposed that the formation of CdO had no detrimental effect on the solar cell performance [41]. In addition, the second peak (located at approx. 531.6 eV for 16 mPa pressure, and 531.9 eV for 20 mPa pressure) is ascribed to SO$_4$ + in the form of CdO [40].

Fig. 6(b) shows the PL and UV-vis (inset) analytical image of the CdS:O film grown at the rate of 0.25 Å/s. At the low energy side of the PL spectra, a broadband around 2.29 eV is attributed to the S vacancy (Vs). There appears a broad high-energy band in the range 2.68 eV related to cadmium atoms located at the interstitial sites [43] and corresponding to the band-to-band transition. The band gap energy of the CdS:O thin films found in PL is nearly the same as the result found from the UV-vis studies (inset of Fig. 6(b) and Table 3). The systematic intense peak at around 1.92 eV in the PL spectra is corresponding to the infrared/red band. The transition happened at this red band may be due to the O complex and/or due to the sulphur vacancy complex, such as CdO as it is found in XPS analysis (Fig. 6(b)(ii)).

The quotient I$_{Vs}$/I$_{bb}$ has been calculated to qualitatively evaluate the “crystalline quality” of the CdS:O thin films. The lower value of I$_{Vs}$/I$_{bb}$ indicates the better “crystalline quality” of the sample. The value of I$_{Vs}$/I$_{bb}$ implies the larger probability for the main radiative transition (band-to-band) as compared to any other transition involving defect states, i.e. sulphur vacancies, interstitial sulfate and so on [44]. As it is observed in Table 3 that the quotient I$_{Vs}$/I$_{bb}$ increases as the O partial pressure increases, which would mean that the local disorder in the films increased resulting in the deterioration of the crystalline quality.

The estimated bandgap using Tauc plot of all CdS:O thin films are shown in Table 3. It is found that the bandgap increases with the decrease of growth rate due to the increase of O content in the films. The increase in the bandgap of CdS:O films may be attributed to an increase in lattice strain owing to decrease in grain size of the films, as also found in the XRD results shown in Table 4. The sensitivity of the bandgap of CdS:O thin films to lattice strain has been reported earlier [45]. XRD pattern of the CdS:O thin films are shown in Fig. 7. The diffraction peaks at 20 positions of 26.61°, 37.08° and 48.02° can be assigned to the planes (002), (102) and (103) of the hexagonal wurzite structure (JCPDS Card No. 01-077-2306). From Table 4, it is observed that the crystallite sizes of the films reduce from 44.92nm to 32.78 nm with the decrease of growth rate that eventually leads to the increase of bandgap. The same effects have also been reported for CdS thin films prepared by CSS in He:O ambient [38] and CdTe:O thin films [46]. With the decrease of growth rate, the density of nucleation centre increases, i.e., low growth rate influence to develop large quantity of nucleation centre of small crystallite size. Defects such as microstrain and dislocation density increase

### Table 3

<table>
<thead>
<tr>
<th>Growth rate (Å/s)</th>
<th>Bandgap (eV)</th>
<th>Cd 3d B.E (eV) at. conc. (%)</th>
<th>S 2p B.E (eV) at. conc. (%)</th>
<th>O 1s B.E (eV) at. conc. (%)</th>
<th>I$<em>{Vs}$/I$</em>{bb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>2.65</td>
<td>411.98 38.15</td>
<td>162.819 32.26</td>
<td>536.050 29.59</td>
<td>0.9</td>
</tr>
<tr>
<td>0.32</td>
<td>2.70</td>
<td>413.149 31.13</td>
<td>170.602 38.43</td>
<td>532.612 30.43</td>
<td>1.1</td>
</tr>
<tr>
<td>0.25</td>
<td>2.72</td>
<td>402.320 27.67</td>
<td>159.913 33.80</td>
<td>532.956 38.52</td>
<td>1.8</td>
</tr>
<tr>
<td>0.15</td>
<td>2.74</td>
<td>409.160 26.57</td>
<td>160.150 29.38</td>
<td>529.974 44.05</td>
<td>1.4</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Growth rate (Å/s)</th>
<th>Peak height, I (111) (a.u)</th>
<th>FWHM, $\theta$ (rad.) ($\times 10^{-3}$)</th>
<th>Crystallite size, D (nm) $\times 10^{-9}$</th>
<th>Micro-strain, $\varepsilon$ ($\times 10^{-3}$)</th>
<th>Dislocation density, $\delta$ ($\times 10^{-14}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>789</td>
<td>3.05</td>
<td>44.92</td>
<td>3.17</td>
<td>4.96</td>
</tr>
<tr>
<td>0.32</td>
<td>593</td>
<td>3.48</td>
<td>39.37</td>
<td>3.62</td>
<td>6.45</td>
</tr>
<tr>
<td>0.25</td>
<td>308</td>
<td>4.18</td>
<td>32.78</td>
<td>4.35</td>
<td>9.30</td>
</tr>
<tr>
<td>0.15</td>
<td>340</td>
<td>3.09</td>
<td>45.02</td>
<td>2.19</td>
<td>2.32</td>
</tr>
</tbody>
</table>
with the decrease of growth rate may be due to the decrease of crystallinity and stoichiometry of the films as evident from XRD pattern and XPS elemental analysis. However, the biggest crystallite size is found for the growth rate of 0.15 Å/s owing to lowest lattice strain [47].

The lowest crystallite size and highest microstrain and dislocation density are observed for the films deposited at a growth rate of 0.25 Å/s, which indicates that the film crystallinity and stoichiometry altered at this stage as the impact of O incorporation. These structural properties may be linked to the amount of CdSO₄ and/or CdO compound developed during the reactive sputtering. The multiple compounds created during the deposition embolden the amorphous nature giving a sign via the reduction of (002) hexagonal peak height. Soo et al. [48] suggested that Cd-S bond length is decreased with the increase of O content in the samples in the case of CdS films prepared in O ambient. As the O content in the sample increases, the coordination number of the nearest S shell around Cd decreases and the local disorder increases, for which the film crystallinity decreases. Moreover, the decreasing coordination number of the nearest S shell around Cd indicates that the CdS:O films are in the form of nanoparticles with decreasing particle size. The decreasing crystallite size leads to the increase of typical quantum confinement effect, which enhances the blue shift in the high energy region and increases the film’s optical bandgap.

Fig. 7(b) shows the resistivity and mobility of the films as the function of growth rate. The highest mobility and resistivity are observed for the film grown at the rate of 0.25 Å/s. According to the XPS results, S:Cd ration increases with the increase of O partial pressure, whereas excessive S increased SO₄ complexes that segregate at the grain boundaries resulting in an increase of the resistivity. Moreover, the quantitative analysis of the XPS results (Table 3) suggests that the films are slightly Cd-poorn. This stoichiometric Cd deficiency could be the cause of the increase in film’s resistivity. However, comparing with the XRD results, it has been found that the resistivity increases with the decrease of film crystallinity. The results are in well agreement with the previously reported results of chemically sprayed CdS thin films [39].

### 3.3. CdTe photovoltaic cell fabrication and performance analysis

Complete photovoltaic devices have been fabricated with the CdTe thin films deposited at the growth rate of 1.8 Å/s, 3.6 Å/s, 4.6 Å/s and 5.4 Å/s on top of “glass/FTO/ZnO:Sn/CdS:O” stacks as the investigation of growth rate effect on photovoltaic cell performance. An HRT ZnO:Sn layer was deposited as the buffer layer by co-sputtering of ZnO (3.0 W/cm²) and Sn (1.0 W/cm²) on soda lime glass and FTO-coated glass substrate at the growth rate of 2.34 Å/s at 300 °C of substrate temperature and 14 mT of working pressure. The growth rate observed during deposition was 2.34 Å/s. The detail optimization process of ZnO:Sn for CdS:O/CdTe solar cell is in progress, and therefore only results relevant to AFM and SEM image are presented in Fig. 8. The surface roughness of the film is found to be 3.07 nm from AFM. The inhomogeneous nano-grains with average grain size of less than 10 nm are observed in the morphology images by SEM. The nanoparticles are distributed uniformly covering the entire surface properly, whereby no voids, pinholes or cracks are observed in the films.

The schematic of the structure FTO/ZnO:Sn/CdS:O/CdTe with a back-contact layer that consists of screen printed Cu-doped graphite (C) buffer, and Ag-paste electrode is shown in Fig. 9(a). The photovoltaic cell J-V characteristics are shown in Fig. 9(b) and the cell performance parameters are shown in Table 5. The cell with CdTe growth rate of 1.8 Å/s is showing very poor efficiency, which may be due to the smaller grain size of CdTe film, i.e. higher grain boundary defects and low carrier concentration as discussed in previous sections. The higher grain boundary reduces the shunt resistance by increasing the recombination and generation on the surface conduction of the cell. It is well known that Cu can easily migrate through the grain boundaries of CdTe to the other layers. Thus, the CdTe films of small grain sizes are easily affected by the Cu migration leading to the shunting effect. Consequently, the Jsc as well as Rsh are observed to increase with the increase of growth rate, which causes bigger grain, low grain boundary effect and better electrical properties of CdTe. The highest Jsc achieved in this study is higher than the previous reported highest efficiency of all-sputtered CdS/CdTe solar cells as shown in Table 5 [10,49], which also indicates the impact of the higher bandgap CdS:O window layer. It should be noticed that, CdS:O film as a window layer implemented to the close space sublimation (CSS) grown CdTe device showed Jsc above 24 mA/cm² [19]. The origin of the Jsc increase can be analysed from external quantum efficiency (EQE) curves. The EQE of the fabricated CdTe solar cells is shown in Fig. 9(c). It has been found that the EQE values in the blue region and UV region became much higher (≥ 50% at 450 nm), probably due to the increased optical transmittance of CdS:O layer. As shown in Fig. 9(c), the EQE curve could be divided into two regions, where region I (400–600 nm) is corresponding to the light absorption as well as the generation, transport and recombination of photogenerated carriers in the pn junction region and region II (600–850 nm) is greatly dependent on the effective transport of photogenerated carriers at the back contact [50]. The QE in the region I is higher for deposition rate of 3.6 Å/s and 4.6 Å/s as attributed to the efficient light absorption and inhibition of carrier recombination. However, the lower values of QE in the region I were found for the deposition rates of 1.8 Å/s and 5.4 Å/s. It should be noticed that the grain boundaries and pinhole were well delineated in those films (Fig. 4), so the possibility of Cu migration through the grain boundaries and pinhole was high that enhanced the recombination of the photogenerated carriers in the p-n junction region. In region II, all cells show decreases of QE indicating to the inefficient formation of back contact, i.e. the CuTe back contact may not be formed sufficiently. In particular, higher QE for cells at CdTe growth rate of 4.6 Å/s was found in the vicinity of 800 nm wavelength region, which contributed to the highest Jsc in this study. However, the increases of carrier recombination at the bulk of CdTe and/or increase of uncompensated impurities in the devices may be the root causes of the decrease of QEs in region II [51]. All in all, Voc and FF are comparatively low found in...
this device. The low Voc and FF may be attributed to the low shunt resistance (Rsh) from the screen printed C:Cu/Ag back contact. Although the Rsh has improved for the high growth rate of CdTe but the cell performance are not found in the satisfactory range, owing to the higher series resistance linked with the ZnO:Sn HRT layer in the front contact. However, the series resistance may also be raised from other factors such as the bulk resistance of the layers and back contact resistance. The high resistive back contact is also visible by the rollover as found in the J-V curves. It is obvious that higher efficiency is attainable in this structure but necessary to optimize the screen printed procedure to create effective ohmic back contact for the CdTe solar cells. It should be noticed that the optimization of ZnO:Sn HRT layer as well as C:Cu screen printed back contact are in progress and significant improvement in cell performance is expected through the contact optimization.

As a whole, the highest conversion efficiency of 10.27% with performance parameters of Voc of 0.67 V, Jsc of 22.6 mA/cm² and FF of 68% have been achieved for the CdTe film growth rate of 5.4 Å/s.

### 4. Conclusion

The effect of growth rate on the structural, electrical and optical properties of CdTe and CdS:O thin films has been extensively investigated by XRD, SEM, AFM, UV–vis, PL, XPS and Hall effect measurement. Considering the films’ crystallite size, texture, dislocation densities, microstrain, and grain size, the optimum sputtering growth rate was found for CdTe film to be 5.4 Å/s. The peaks of TeO₂ and Te in the CdCl₂ heat treated films indicate that preferred Te-rich surface is developed through the process. Oxygen (O) content on the CdS:O films varied with the variation of growth rate as well as ambient pressure. XPS analysis shows that the CdS:O film is the conglomerate of CdS, CdSO₄, and CdO compounds, where the compositions and optoelectronic properties varied with the growth rate. Optimized CdS:O film properties for the buffer layer application was found at the growth rate of 0.25 Å/s. The complete cell was fabricated with the screen printed copper doped graphite paste and silver metal (C:Cu/Ag) back contact with the configuration of FTO/ZnO:Sn/CdS:O/CdTe/C:Cu/C/Ag on glass.

Table 5: Solar cell performance of SLG/FTO/ZnO:Sn/CdS:O/CdTe/C:Cu/Ag configuration (cell area 0.25 cm²), in comparison with all sputtered CdTe solar cell configurations of *ASG/FTO/CdS/CdTe/Cu/Au [9] and #SLG/FTO/CdS/CdTe/Cu/Au [49].

<table>
<thead>
<tr>
<th>Growth rate (CdTe) (Å/s)</th>
<th>Growth rate (CdS:O) (Å/s)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
<th>Rs (Ω·cm²)</th>
<th>Rsh (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8 Å/s</td>
<td>0.25 Å/s</td>
<td>0.56</td>
<td>18.6</td>
<td>59</td>
<td>6.2</td>
<td>4.1</td>
<td>348</td>
</tr>
<tr>
<td>3.6 Å/s</td>
<td>0.72 Å/s</td>
<td>0.72</td>
<td>20.1</td>
<td>65</td>
<td>9.4</td>
<td>3.3</td>
<td>798</td>
</tr>
<tr>
<td>4.6 Å/s</td>
<td>0.67 Å/s</td>
<td>0.67</td>
<td>22.6</td>
<td>68</td>
<td>10.3</td>
<td>4.8</td>
<td>568</td>
</tr>
<tr>
<td>5.4 Å/s</td>
<td>0.68 Å/s</td>
<td>0.68</td>
<td>21.9</td>
<td>62</td>
<td>9.2</td>
<td>5.1</td>
<td>596</td>
</tr>
<tr>
<td>*CdTe = 2.3 µm</td>
<td>CdS = 0.13 µm</td>
<td>0.82</td>
<td>20.7</td>
<td>73.9</td>
<td>12.6</td>
<td>3.9</td>
<td>1822</td>
</tr>
<tr>
<td>*CdTe = 2.0 µm</td>
<td>CdS = 0.25 µm</td>
<td>0.81</td>
<td>19.7</td>
<td>73.3</td>
<td>11.6</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* CdTe = 2.3 µm CdS = 0.13 µm
# CdTe = 2.0 µm CdS = 0.25 µm

Fig. 9. (a) Schematic of the solar cell structure, (b) J-V curves of the ZnO:Sn/CdS:O/CdTe/Cu/C/Ag solar cell with respect to the growth rate, and (c) external quantum efficiency (EQE) of the solar cells.
These results thus showed the dependence of solar cell performance on CdTe thin film growth rate on magnetron-sputter deposition as well as cells’ contact characteristics. The highest photovoltaic efficiency of 10.3% was so far achieved for the CdTe growth rate of 5.4 Å/s and CdS:O growth rate of 0.25 Å/s, respectively.

Acknowledgment

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References