

How to control the stoichiometry of cadmium telluride thin film for photovoltaic applications

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In this study, Bube's growth model for a cadmium telluride (CdTe) polycrystalline thin film was re-examined with a view of avoiding his assumptions that neglect the vapor pressures of Cd and Te₂ near the film. We proposed a new thermodynamic growth model based on the fact that there is an experimentally verified characteristic ratio (α) of equilibrium partial pressures $P_{Cd}/2P_{Te2}$ that depends on the temperature T and CdTe stoichiometry. By writing $P_{Cd}(0) = 2\alpha(0)P_{Te2}(0)$ and $P_{Cd}(h)$ $= 2\alpha(h)P_{Te2}(h)$, where $\alpha(0)$ is determined by source stoichiometry, we can solve the equations for $\alpha(h)$ and thereby determine the stoichiometry of the CdTe thin film grown under physical vapor deposition (PVD) conditions. Simulation was performed to predict the stoichiometry of the CdTe thin film as a function of source stoichiometry for various source-film temperature combinations. The results show that for a typical CdTe PVD process with $T_{source} > T_{thinfilm}$: (1) stable deposition, without a non-stoichiometric composition shift, can be achieved at congruentgrowth stoichiometry; (2) any stoichiometric deviation from the congruent sublimation point becomes more substantial (in the same direction) in the thin film than in the source; and (3) larger ΔT between the source and the thin film results in a more composition shift. Published by AIP Publishing. https://doi.org/10.1063/1.4995655

I. INTRODUCTION

Cadmium telluride (CdTe) thin film photovoltaic (PV) technology has demonstrated its commercial success and great potential in the solar energy industry. CdTe is a group II–VI semiconductor with bipolar intrinsic doping capability.¹ The electrical properties of non-doped CdTe depend sensitively on the compound stoichiometry. The non-stoichiometric CdTe film results in either n- or *p*-type conductivity.² While excess Cd yields n-type conductivity, excess Te produces *p*-type films.

CdTe thin film solar cells are fabricated as a hetero-junction structure, in which the CdTe layer is usually *p*-type acting as a photoabsorbing layer to generate carriers. In the last 30 years, most CdTe photovoltaics (PV) technologies have been using Te-rich CdTe. Some experts in the field believed that at a given temperature, the higher vapor pressure of Cd than that of Te₂ causes loss of Cd during deposition, and the deposited CdTe becomes Te-rich even if the source material is stoichiometric.^{3,4} For CdTe, substantial gains in carrier concentration rely on external doping. The most commonly used extrinsic doping in Te-rich CdTe is copper. However, PV technologies based on Te-rich CdTe have failed to produce a hole density greater

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063505-2 Tan et al.

than 10^{15} cm^{-3} , resulting from self-compensation, low carrier lifetime due to Te_{Cd} antisite deep levels, and the stability issue induced by Cu migration. These have contributed to the stagnation of open-circuit voltage (V_{OC}) for 30 years. The recent breakthrough in monocrystalline CdTe solar cells with V_{OC} breaking 1 V barrier demonstrated a new direction of the technology by shifting to a Cd-rich stoichiometry.⁵ Through external doping with group V elements, e.g., P or As, Cd-rich CdTe can be turned into *p*-type with hole densities exceeding 10^{17} cm^{-3} . Potentially, PV technologies based on Cd-rich CdTe may play an extremely important role in the future product market of CdTe solar panels.

It should be mentioned that favorable stoichiometry of CdTe is prerequisite for extrinsic doping to be effective. For Te-rich CdTe, the presence of intrinsic defects V_{Cd} enables *p*-type Cu doping by placing Cu onto the Cd sites to form substitutional Cu_{Cd} .^{6–8} For Cd-rich CdTe, the presence of intrinsic defects V_{Te} enables *p*-type P doping by placing P onto the Te sites to form substitutional P_{Te} .⁶ Clearly, stoichiometry of CdTe is one important factor determining not only the intrinsic electrical properties but also the processing procedures that enable the fabrication of high performance thin film PV devices.

The CdTe polycrystalline thin films are usually accomplished by physical vapor deposition (PVD). Until recently, the theory and modeling of the PVD process, either close-space sublimation (CSS) or vapor-transport deposition (VTD) of the CdTe polycrystalline thin film, however still have some fundamental flaws. The stoichiometric growth condition was incorrectly expressed in several studies, where the stoichiometric condition of CdTe thin film growth was modeled as $P_{Cd} = 2P_{Te2}$ both near the source and near the thin film.^{9,10} As the model only considers the reversible dissociation and recombination of $CdTe(s) \leftrightarrow Cd(g) + 1/2Te_2(g)$, such a fixed pressure ratio of 2 lacks theoretical as well as experimental groundings.

The correct stoichiometric condition of CdTe thin film growth was previously expressed as $J_{Cd} = 2J_{Te2}$ by Bube *et al.*¹¹ and by Chin *et al.*,¹² where J_{Cd} and J_{Te2} are the diffusive fluxes of Cd and Te₂, respectively, from the source to the superstrate (substrate) where the CdTe thin film is deposited. In the present work, we re-visit their growth models. After reviewing and discussing their drawbacks, we propose an improved thermodynamic model by introducing an equation of $P_{Cd} = 2\alpha P_{Te2}$, where α is a characteristic ratio between P_{Cd} and $2P_{Te2}$, determined by CdTe stoichiometry and the temperature. Our growth model achieves an appropriate solution to determine the α value near the thin film. This allows us to predict and thus enables us to control the stoichiometry of the CdTe thin film as a function of CdTe source stoichiometry. The results of simulation are shown for various source-film temperature combinations.

II. THEORETICAL MODELING OF CdTe THIN FILM GROWTH

A model of CSS CdTe thin film growth was proposed by Bube *et al.* in 1984.¹¹ In their modeling, the stoichiometric condition was correctly expressed as

$$J_{Cd} = 2J_{Te2},\tag{1}$$

where J_{Cd} and J_{Te2} are the diffusive fluxes of Cd and Te₂, respectively, from the source at z = 0 to the superstrate at z = h and h is the spacing between the source and the superstrate on which the CdTe thin film is being deposited. In Bube's approach, there were 4 unknowns: $P_{Cd}(0)$, $P_{Te2}(0)$, $P_{Cd}(h)$, and $P_{Te2}(h)$ but only 3 equations, i.e., the equation of the stoichiometric condition and the two equations of chemical reaction equilibrium near the source (0) and near the thin film (h)

$$K(0) = P_{Cd}(0)\sqrt{P_{Te2}(0)} = \exp\left[\frac{-\Delta G_{CdTe}(T_0)}{RT_0}\right],$$
(2)

$$K(h) = P_{Cd}(h)\sqrt{P_{Te2}(h)} = \exp\left[\frac{-\Delta G_{CdTe}(T_h)}{RT_h}\right],$$
(3)

where R is the gas constant and $\Delta G_{CdTe}(T)$ is the Gibbs free energy change at a given temperature T. The steady-state diffusive fluxes of Cd and Te₂, under diffusion-limited transport conditions, are described by Fick's first law 063505-3 Tan et al.

J. Renewable Sustainable Energy 9, 063505 (2017)

$$J_{Cd} = \frac{D_{Cd}}{RhT_{avg}} \left[P_{Cd}(0) - P_{Cd}(h) \right],$$
 (4)

$$J_{Te2} = \frac{D_{Te2}}{RhT_{avg}} \left[P_{Te2}(0) - P_{Te2}(h) \right],$$
(5)

where T_{avg} is the average temperature of the source and the thin film in units of K and D_{Cd} and D_{Te2} are the diffusion coefficients of Cd and Te₂, respectively, in units of m² s⁻¹. As carrier gas, such as He or Ar, has usually been used during CSS CdTe deposition, the system can be treated as a binary gas diffusion system of Cd/carrier gas or Te₂/carrier gas. The diffusion coefficients of Cd and Te₂ in the binary system $D_{i,j}$ can be expressed in the Stefan-Maxwell form¹³

$$D_{i,j} = \frac{3kT_{avg}}{8P_{total}\sigma_{ij}^2} \sqrt{\frac{kT_{avg}}{2\pi} \left(\frac{1}{m_i} + \frac{1}{m_j}\right)},\tag{6}$$

where *i* indicates Cd or Te₂, *j* indicates the selected carrier gas, *k* is the Boltzmann constant in units of J K⁻¹, P_{total} is the total pressure in units of Pascal, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ is the average collision diameter in units of meter, and *m* is the molecular (atomic) weight in units of kilogram.

To resolve the difficulty of 4 unknowns with 3 equations, Bube *et al.* assumed that over the temperature range typically used during CSS CdTe growth, the vapor pressures of Cd and Te₂ near the thin film could be neglected, i.e., $P_{Cd}(0)$, $P_{Te2}(0) \gg P_{Cd}(h)$, $P_{Te2}(h)$, if the temperature difference between the source and the film (ΔT) was 70 °C or larger. This in turn introduced an additional equation of

$$2 = \frac{D_{Cd,j} P_{Cd}(0)}{D_{Te2,j} P_{Te2}(0)},\tag{7}$$

which allowed them to solve the set of equations and thus yield the CdTe growth rate as a function of growth conditions.

There are two major drawbacks in Bube's work. First, the assumption of $P_{Cd}(0)$, $P_{Te2}(0) \gg P_{Cd}(h)$, $P_{Te2}(h)$ does not hold true, as shown by experimental measurements of Cd and Te₂ partial pressures of Cd_{1+x}Te_{1-x} over a relatively wide temperature range.¹⁴ Second, the work only investigated the effects of deposition conditions on the growth rate but not on the stoichiometry of the CdTe thin film. Modeling for the deposition rate of CdTe has been studied quite extensively, considering both diffusion limited and sublimation limited cases.¹⁰ Considering the advanced technologies nowadays to accurately measure the film thickness both *in-situ* and *ex-situ*, it is rather more imperative to model and to predict the CdTe thin film stoichiometry. It is worth noting that a non-stoichiometric composition shift of 0.001 at. % in CdTe may have strong influences on the actual carrier density. Such a level of changes in stoichiometry may be beyond the detection limit of any experimental methods.

Recently, our research group has demonstrated a novel and convenient method to resolve the difficulty of 4 unknowns with 3 equations encountered in Bube's work, by treating CdTe with a small deviation from the perfect stoichiometry as a solid solution of excess pure Te or Cd solute in congruently grown CdTe solvent.¹² In that growth model, we introduced 1 extra unknown, the excess amount of solute in the CdTe thin film $\delta(h)$, but 2 additional equations which are the two polynomial equations of partial pressures based on Henry's law near the source (0) and near the film (h)

$$P_{i} = H_{0}(i,T) + \delta(h)H_{1}(i,T) + \delta(h)^{2}H_{2}(i,T),$$
(8)

$$P_i = H_0(i,T) + \delta(0)H_1(i,T) + \delta(0)^2 H_2(i,T),$$
(9)

where i indicates Cd or Te₂ and H s are the coefficients of polynomials that are functions of temperature. Our previous model was based on the data of experimentally measured equilibrium

063505-4 Tan et al.

partial pressures of Cd and Te₂ in the binary Cd-Te system as a function of CdTe source stoichiometry,¹⁴ and the coefficients of polynomials for P_{Cd} or P_{Te2} were obtained by best fitting of experimental data using the polynomial functions. With the excess amount of solute in CdTe source $\delta(0)$ being known, determined by source stoichiometry, we were able to solve the equations and obtain the corresponding value of $\delta(h)$ for the CdTe thin film grown under PVD conditions.

Perhaps, the most significant advance in our previous modeling work was that the stoichiometry of the CdTe thin film under PVD growth was shown to be determined by the stoichiometry of the CdTe source as well as the growth condition. This dependence was preliminarily demonstrated for one source temperature and three different thin film temperatures. Following our previous work, we found it worthwhile to present a dedicated work, which models and predicts the stoichiometry of the CdTe thin film as a function of the source stoichiometry, for a wider range of temperatures that will be commonly used for a typical CdTe PVD deposition. The potential results should be highly useful in the field of CdTe PV technologies. The scientists and engineers could use the work as a guidance to fine tune the growth parameters and source stoichiometry, aiming to reach a desired CdTe thin film stoichiometry.

In the present work, Bube's growth model for CdTe is re-examined with a view of avoiding his assumptions to solve the equations. Our previous assumption of using Henry's law despite its convenience—will also be avoided because it has not been experimentally proved that the CdTe deviated slightly from the perfect stoichiometric condition that can be depicted as the solid solution obeying Henry's law. To balance the number of equations and the number of unknowns, we herein introduce an equation correlating the equilibrium partial vapor pressures of Cd and Te₂. This equation is based on the fact that there is an experimentally verified characteristic ratio (α) of $P_{Cd}/2P_{Te2}$, which depends on the temperature T and CdTe stoichiometry.¹⁴ For a given source-film temperature combination, our model provides two additional equations

$$P_{Cd}(0) = 2\alpha(0)P_{Te2}(0), \tag{10}$$

$$P_{Cd}(h) = 2\alpha(h)P_{Te2}(h), \tag{11}$$

but one extra unknown $\alpha(h)$. With $\alpha(0)$ being given by the source stoichiometry, we are able to solve the 5 equations with 5 unknowns, rendering the dependence of $\alpha(h)$ as a function of $\alpha(0)$. It is interesting to note that the dependence of $\alpha(h)$ on $\alpha(0)$ is equivalent to the dependence of $\delta(h)$ on $\delta(0)$.

III. FITTING OF EXPERIMENTAL DATA AND LOW-TEMPERATURE EXTRAPOLATION

In our previous work, we used polynomial functions based on Henry's law to fit the experimental data of equilibrium partial vapor pressures of Cd and Te₂ published by Greenberg.¹⁴ However, the method that was used to extrapolate polynomial coefficients for vapor pressures at lower temperatures lacks a physical grounding as well as the necessary accuracies. In the present work, a numerical method is adopted to fit the experimental data of Cd and Te₂ partial vapor pressures as a function of CdTe stoichiometry. First, the experimental data, measured at temperatures of 1073 K, 1123 K, 1173 K, and 1223 K, were obtained by digitizing the figures published by Greenberg. The digitized graphs were then tabulated in the range of 49.997–50.007 at. % Te with an interval of 0.0001 at. %, using the "smooth spline" function provided by Matlab. Such a method does not force the data to follow any analytical formula but rather simply follow any arbitrary data trend. As shown in Fig. 1, the tabulated data satisfactorily match the graph published by Greenberg.

It is worth discussing that under thermodynamic equilibrium, the solid phase composition [at. % Te] can be significantly different from that of the vapor phase $[2P_{Te2}/(P_{Cd} + 2P_{Te2})]$. According to the experimental data published by Greenberg (shown as solid symbols in Fig. 1), while there is still nearly 50% Te in the CdTe solid, the vapor composition is almost free of Te







FIG. 1. Fitting the experimental data of equilibrium partial vapor pressures of Cd and Te_2 as a function of CdTe stoichiometry using a numerical method. The tabulated data of vapor pressures match the experimental results satisfactorily.

when at.% Te < 49.999% in the solid and is almost free of Cd when at. % Te > 50.007% in the solid. As a result, it is very difficult to obtain an accurate reading of a low partial pressure, while the other component is dominant in the vapor phase. Consequently, thermodynamic confinement obeying Eq. (2) was applied to obtain the partial pressure values for the negligible vapor component, while the partial pressure values for the dominant component were directly tabulated from the Greenberg graph.

To extrapolate the vapor pressures at lower temperatures for each tabulated stoichiometry, we used the well-known Antoine equation

$$\log_{10}P = A - \frac{B}{T} \,. \tag{12}$$

The Antoine equation is a class of semi-empirical correlations describing the relationship between vapor pressure and temperature for pure components.¹⁵ Here, we treated each stoichiometry of CdTe as a single component.

IV. RESULTS AND DISCUSSION

Figure 2 summarizes the calculated values of $\alpha(h)$ as a function of $\alpha(0)$ for various CdTe source temperatures in the range of 900–1180 K. For each source temperature, $\alpha(h)$ values were calculated at five different film temperatures to demonstrate the effect of temperature conditions. The source-film temperature combinations were selected to be relevant to a typical CSS or VTD deposition of CdTe thin films. For each CdTe source temperature, the five different film temperatures correspond to $\Delta T (= T_{source} - T_{thinfilm})$ values of 20, 60, 100, 140, and 180 K, respectively.

Given the characteristic correlation between the value of α and the stoichiometry of CdTe at a given temperature, the plots of $\alpha(h)$ versus $\alpha(0)$ can be replotted as CdTe film stoichiometry versus CdTe source stoichiometry, with the results being shown in Fig. 3. The characteristic



FIG. 2. The dependence of $\alpha(h)$ on $\alpha(0)$ for various source temperatures in the range of 900 K–1180 K. For each source temperature, $\alpha(h)$ values were calculated at five different film temperatures.

063505-7 Tan et al.

J. Renewable Sustainable Energy 9, 063505 (2017)



FIG. 3. The dependence of CdTe thin film stoichiometry on CdTe source stoichiometry. The results are shown for various source-film temperature combinations.

063505-8 Tan et al.

correlations at temperatures of 1073, 1123, 1173, and 1223 K were extracted from the experimental data of partial pressures published by Greenberg. The characteristic correlations at other temperatures were obtained by extrapolation of partial pressures using the Antoine equation. As shown in Fig. 3, the stoichiometry of the CdTe source or thin film was modeled in the range of 49.995–50.004 at. % Te for consideration of CdTe thin film PV applications. Further deviation from the perfect CdTe stoichiometry would result in precipitation of the elemental Cd or elemental Te phase. The supersaturated solid solution would segregate into a two-phase microstructure with elemental inclusion in the matrix of the CdTe compound.

Close inspection of Figs. 2 and 3 reveals that there is an inflection point in the curve of $\alpha(h)$ vs. $\alpha(0)$ or in the curve of CdTe film stoichiometry vs. source stoichiometry. Near the inflection point, the α ratio of $P_{Cd}/2P_{Te2}$ or the stoichiometry of CdTe shows minimal changes comparing the thin film with the source. This inflection point is positioned on the Te-rich side of stoichiometry in both vapor and solid phases. This observation suggests that the inflection point is near the congruent-growth stoichiometry rather than near the point of perfect CdTe solid stoichiometry or the point of vapor phase stoichiometry. From the calculated results, stable deposition, without the non-stoichiometric composition shift, in principle can be achieved at the congruent-growth stoichiometry. However, as the congruent-sublimation point also shifts with temperature, the CdTe source temperature needs to be controlled in accordance with the source stoichiometry so that a stable deposition without the composition shift can be really achieved.

As shown in Figs. 2 and 3, on either side of the congruent-growth stoichiometry, any stoichiometric deviation from the congruent sublimation point becomes more substantial (in the same direction) in the CdTe thin film than in the CdTe source. This modeling result is important for a typical CdTe PVD process with source temperature higher than film temperature. The commonly used CdTe source material with the composition close to the perfect CdTe stoichiometry is likely to position on the Te-deficient side of congruent-growth stoichiometry. Consequently, for a typical CdTe PVD process, there is a non-negligible shift of CdTe stoichiometry that is however being usually neglected in the field of CdTe thin film PV technologies.

Another point observed from Figs. 2 and 3 is that larger ΔT between the source and the thin film during a process of PVD results in a more shift in stoichiometry from the CdTe source to the CdTe thin film. For each source temperature, while the value of ΔT being close to zero, the plot of $\alpha(h)$ vs. $\alpha(0)$ or film stoichiometry vs. source stoichiometry shows a correlation of linear dependency. This linear relation makes sense as the partial vapor pressures of Cd or Te₂ remain similar on either side of the source or the thin film, leading to minimal changes in CdTe stoichiometry. As the value of ΔT increases, apart from the change in partial vapor pressures, there is also a stronger shift in the characteristic correlation between the value of α and the stoichiometry of CdTe. As a result, any stoichiometric deviation from the inflection point becomes more substantial in the CdTe thin film as the temperature difference ΔT increases.

It should be noted that our calculated results have introduced a new considering point among the effects of growth temperature for CdTe thin film PV applications. In general, the thin film growth temperature at the superstrate (substrate) level was believed to affect the quality of the CdTe polycrystalline thin film, including the grain size, the defect density, and the film surface morphology.¹⁶ It has also been reported that CdTe thin films deposited at lower substrate temperature show a high degree of porosity between the columnar grain structures.¹⁷ Considering these points, it was argued that a higher growth temperature is more beneficial for growing polycrystalline films with fewer defects. On the other hand, a lower growth temperature is sometime beneficial from practical viewpoints. For example, a low-temperature solar module fabrication process is needed to accommodate the low strain point of the soda-limeglass superstrate. As demonstrated by the calculated results of the present study, the temperature difference ΔT in principle will also affect the stoichiometry of the CdTe thin film grown under PVD conditions. Since a non-stoichiometric composition shift in CdTe may have strong influences on the actual carrier density, it is imperative to consider the temperature effect on 063505-9 Tan et al.

stoichiometry while controlling the temperature condition of a deposition process. As the temperature effect on stoichiometry was usually neglected, this makes our work new and useful to the field of CdTe PV technologies.

Derived from the results shown in Fig. 3, we have made a master plot of the CdTe composition shift as a function of increasing ΔT , which enables us to predict the stoichiometry of the CdTe thin film deposited at a certain source-film temperature combination. As the dependence of composition shift vs. ΔT appears to be linear, the slope and intercept of each line at a given source temperature can be extrapolated using the fitted lines shown in Figs. 4(b) and 4(c), respectively. Assuming that the stoichiometry of the CdTe source is known, we can therefore control the stoichiometry of the CdTe thin film by fine tuning the temperature condition of a PVD process, using the information provided in Fig. 4.

Finally, it is important to discuss the limitations of our growth model. The system under consideration is assumed to reach thermodynamic equilibrium for both the CdTe source and the CdTe thin film. Effects from kinetic points of view are thus not considered. This assumption of thermodynamic equilibrium is probably more valid for a deposition process using CSS than using VTD. The kinetics of vapor transport should play a major role in the mechanism of the VTD process. Second, complicated situations encountered in reality are not considered in our growth model. For example, O₂ is sometimes added to the carrier gas to enhance certain properties of CdTe PV devices.¹⁸ The oxygen in the carrier gas however will consume Cd by forming CdO, making the system more Te-rich. Moreover, Cd atoms are more likely to leak out from the edge of the crucible due to the higher diffusivity of Cd atoms than Te₂ molecules. Consequently, the non-stoichiometric composition shift in CdTe under PVD conditions is driven not only by thermodynamics but also by several issues of processing controls.



FIG. 4. (a) Master plot of the CdTe composition shift (% film – % source), on the Cd-excess side of the congruent point, as a function of increasing ΔT , for various source temperatures from 900 to 1180 K. As the dependence appears to be linear, the slope and intercept of each line (at a given source temperature) shown in the master plot can be calculated using the equations shown in (b) and (c), respectively. This allows us to predict the stoichiometry of the CdTe thin film deposited at a certain source-film temperature combination.

063505-10 Tan et al.

V. CONCLUSION

The technologies employed for CdTe thin film photovoltaics are strongly dependent on the exact stoichiometry of CdTe thin films. It is important to foresee the stoichiometry of CdTe films grown under PVD conditions, thereby being able to determine the techniques that should be used during the processing steps. As the deviation from the perfect stoichiometry is most likely too small to be accurately measured using existing analytical instruments, a growth model that predicts and controls the CdTe thin film stoichiometry is highly useful. In this study, we reported an improved thermodynamic model for CdTe thin films grown under PVD conditions. This model considers a characteristic ratio (α) of equilibrium partial pressures $P_{Cd}/2P_{Te2}$ that depends on the temperature T and CdTe stoichiometry. By introducing two equations $P_{Cd}(0) = 2\alpha(0)P_{Te2}(0)$ and $P_{Cd}(h) = 2\alpha(h)P_{Te2}(h)$, where $\alpha(0)$ is determined by the source stoichiometry, we can solve the equations for $\alpha(h)$ and thereby determine the stoichiometry of the CdTe thin film. Simulation was performed to predict the stoichiometry of the CdTe thin film as a function of source stoichiometry for various source-film temperature combinations. The results show that for a typical CdTe PVD process with $T_{source} > T_{thinfilm}$: (1) Stable deposition, without the non-stoichiometric composition shift, can be achieved at the congruent-growth stoichiometry; (2) any stoichiometric deviation from the congruent sublimation point becomes more substantial (in the same direction) in the thin film than in the source; and (3) larger ΔT between the source and the thin film results in a more composition shift. In a separate work, we intend to design and implement laser absorption spectroscopy to continuously monitor the Cd and Te₂ partial pressures from the CdTe solid. This would be an *in-situ* technique but to monitor the stoichiometry of the CdTe compound indirectly. The technique can be useful to ensure that the growth model we established here is correct and can be utilized to optimize the stoichiometry of CdTe thin films for PV applications.

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