Nonstoichiometric composition shift in physical vapor deposition of CdTe thin films

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While it is being debated whether Cd vacancy is an effective p-dopant in CdTe, and whether CdTe thin film in solar energy application should be Cd-deficient or Cd-rich, in the theory of CdTe physical vapor deposition (PVD) it has been assumed that both the source material and the thin film product is stoichiometric. To remediate the lack of effective theory, a new PVD model for CdTe photovoltaic (PV) modules is presented in this work, in which the composition of the CdTe thin film under growth is a parameter determined by the source CdTe composition as well as the growth condition. The solid phase \textit{Cd}_{1−δ}\textit{Te}_{1−δ} compound under deposition temperature is treated as a solid solution with \textit{n} mole of excess pure Te or Cd as solute and one mole of congruently grown CdTe as solvent. Assuming that the vapor pressure of Te\textsubscript{2} can be calculated by using the law of solid solution \textit{P}_{Te\textsubscript{2}}=\textit{H}_{0}+\textit{a}\textsubscript{Te}\textsubscript{2}\textsubscript{δ}\textsubscript{H}_{2} round the congruent composition, where the molar number \textit{a} and the constants \textit{H}_{0}, \textit{H}_{1} and \textit{H}_{2} as functions of temperature \textit{T} are extracted from the experimental data. Thus, the mole fraction of solute in the grown CdTe thin film as well as the growth rate, as a function of the solute mole fraction in the source CdTe can be determined.

1. Introduction

Physical vapor deposition (PVD) of CdTe thin film is widely used in photovoltaic (PV) module production. So far in the close-spaced sublimation (CSS) PVD modeling of CdTe as well as other semiconduc-

tor compounds, it is assumed that both the source material and the thin film product are stoichiometric [1,2]. The diffusion-limited growth model of CSS was discussed by Bube et al. [1] in detail, where the ratio of the fluxes of Cd atoms and Te\textsubscript{2} molecules from the source to the substrate were assumed to be 2:1 in order to get stoichiometric CdTe films. This assumption is accurate enough for the calculations of the growth rate. It is well known, however, that the minor deviation of the composition of thin film CdTe from its perfect stoichiometric crystal has major effect on its electronic properties [3]. A question arises: Is it possible to find the proper temperatures and background pressure, as well as a source material—for example the Cd-deficient (or Te-rich)—with the proper ratio of Cd/Te so that the grown CdTe thin film product has the optimized Cd/Te ratio and electronic properties?

From the fitted PTX curves by Greenberg [4], the partial pressure curves of Cd and Te\textsubscript{2} as a function of non-stoichiometry under each temperature cross each other at a particular composition, very close to the congruent sublimation point. The cross point of the two partial pressure curves is always at Te rich side, making CdTe films grown by CSS always Cd-deficient (or Te-rich). The CdTe compound (denoted as \textit{Cd}_{1−δ}\textit{Te}_{1−δ}) were considered as a function of atomic percentage of Te in the PTX works of Greenberg, where the atomic fraction number of Te \textit{F}_{Te} is linked to \textit{x} as \textit{F}_{Te}=\textit{x}/2. The solid CdTe compound can be treated as a solid solution with either stoichiometric CdTe as solvent and excess pure Te atoms as solute, or congruently-grown CdTe (Te rich) as solvent and excess Cd or Te as solute. The molar number \textit{a} is defined as the mole concentration of the solute in one mole solvent. Assuming that the partial vapor pressures obey the law of solid solution \textit{P}_{\textit{Cd} or \textit{Te}2}=\textit{H}_{0}+\textit{a}\textsubscript{\textit{Cd} or \textit{Te}2}\textsubscript{δ}\textsubscript{H}_{2}, where the molar number \textit{a} of the solvent and the constants \textit{H}_{0}, \textit{H}_{1} and \textit{H}_{2} as functions of temperature \textit{T} can be extracted from the experimental data and will be discussed below. Therefore, the answer to the question seems to be positive.

2. Results and discussion

This part is organized around three different sections. First, a thermodynamic model is introduced to discuss how excess Cd and Te is treated as the solute in a solvent comprised of vapor phase stoichiometric, solid phase stoichiometric and congruent PVD conditions. Next, we consider congruent PVD condition as the...
solvent and refine this model using PTX partial pressure data published by Greenburg [4]. Lastly, we use this model to calculate the resulting composition of films deposited by close-spaced sublimation, by assuming different source material stoichiometry.

2.1. Nonstoichiometric compound solid solution model

According to the classic Henry's law, the saturated vapor pressure of solute B in a solution is

$$P_B = \gamma_B X_B P_B^0 = H_1 X_B$$

where $X_B$ is the molar number of the solute, $P_B^0$ the saturated vapor pressure of pure B, and $\gamma_B$ the activity coefficient of solute B dissolved or dispersed in solvent A. If the attraction among solute atoms is greater than that between the solute atom B and the solvent atom A, $\gamma_B$ is less than 1. Otherwise, $\gamma_B$ is greater than 1. Combining $P_B^0$ and $\gamma_B$, we have $H_1$, which is independent of $X_B$. For solution with very low solute concentration, $X_B \ll 1$, we have a constant linearity coefficient $H_1$, as shown in Eq. (1). To simplify discussion, we start with an A-deficient or B-rich compound semiconductor AB, the cation element A and the anion element B being volatile. There are three special points, as shown in Fig. 1, in the diagram of saturated vapor pressures of A and B under solid–vapor equilibrium condition at an elevated temperature $T$.

(1) Point V—vapor phase stoichiometric

$P_A = P_B$, or molar number $X_A = X_B$ in vapor phase, but nonstoichiometric in solid phase as shown by its composition $A_{1-\delta} B_{1+\delta}$

$$A_{1-\delta} B_{1+\delta} = (1-\delta) A + (1+\delta) B - \Delta G_V$$

with $P_{AV} = P_{BV}$ satisfying

$$P_{AV}^{1-\delta} P_{BV}^{1+\delta} = P_{AV} P_{BV} = \exp\left(\frac{-\Delta G_V}{RT}\right)$$

(2) Point S—solid phase stoichiometric

Stoichiometric AB or $X_A = X_B$ in solid phase, but nonstoichiometric in vapor phase with $P_A > P_B$; or $X_A > X_B$

$$A B = A + B - \Delta G$$

with $P_{AS} > P_{BS}$ satisfying

$$P_{AS} P_{BS} = \exp\left(-\frac{\Delta G}{RT}\right)$$

(3) Point C—congruent PVD condition, with same molar composition in solid as well as vapor phase, C being at right and very close to V

$$A_{1-\delta} B_{1+\delta} = (1-\delta) A + (1+\delta) B - \Delta G_C$$

with $P_{AV}^{1-\delta} P_{BV}^{1+\delta} = \exp\left(\frac{-\Delta G_C}{RT}\right)$

The PVD source material as well as the desired nonstoichiometric compound thin film product $A_{1-\delta} B_{1+\delta}$ is, however, not of the composition V, S or C. Although much smaller than 1, $\alpha$ may be much greater than $\delta\nu_0$ or $\delta\chi$. For a A-deficient or B-rich compound, we hypothesize that $A_{1-\delta} B_{1+\delta}$ may behave as a solid solution with solute B “dissolved” in the solvent AB, or a solid solution with excess A or B “dissolved” in the solvent $A_{1-\delta} B_{1+\delta}$. As a phenomenological hypothesis, which is based on empirical data, the solid solution may have all 3 forms of the compound as solvents. The 3 cases in the B-rich compound are (in the format of normalized solvent+molar number $a \times$ solute):

$$A_{1-\delta} B_{1+\delta} \Rightarrow AB + \frac{2\delta}{1-\delta} B$$

$$A_{1-\delta} B_{1+\delta} \Rightarrow \left\{ \begin{array}{ll} A_{1-\delta} B_{1+\delta} + \frac{2\delta - \delta\chi}{1-\delta} B & (\text{if } \delta > \delta\chi) \\ A_{1-\delta} B_{1+\delta} + \frac{2\delta - \delta\nu_0}{1-\delta} A & (\text{if } \delta < \delta\nu_0) \end{array} \right. \right.$$

$$A_{1-\delta} B_{1+\delta} \Rightarrow \left\{ \begin{array}{ll} A_{1-\delta} B_{1+\delta} + \frac{2\delta - \delta\chi}{1-\delta} B & (\text{if } \delta > \delta\chi) \\ A_{1-\delta} B_{1+\delta} + \frac{2\delta - \delta\nu_0}{1-\delta} A & (\text{if } \delta < \delta\nu_0) \end{array} \right. \right.$$
It is clear that under thermodynamic equilibrium, the solid phase composition (shown by Te atomic fraction number $F_{Te}$) is very different from that of the vapor phase $[\frac{F_{Te}}{2P_{Te}}]/(P_{Cd}+2P_{Te})$.

According to the experimental data at 1073 K, the vapor’s composition will become almost Te free when $F_{Te} \leq 49.996\%$ in the source solid, and will become almost Cd free when $F_{Te} \geq 50.008\%$ in the source solid, although there is still nearly 50% Te in the solid. The law of solute vapor pressure is applicable because the molar number $a$ of solute $<1$ in such solid composition range.

This behavior is similar regardless whether the solid CdTe compound is related as a solid solution with either stoichiometric CdTe as the solvent and excess Te as solute, or congruently-grown CdTe (Te-rich) as the solvent and excess Cd or Te as the solutes. Although it is unknown which the solvent physically exists, its data still can be treated. Judging from the experimental data, more accurate pressure reading is achieved when one component is dominant and the other is negligible (e.g. $P_{Cd}$ reading is more accurate when $P_{Cd} \gg P_{Te}$). For symmetrical reason, we choose point $V$ as the solvent composition, which is close to congruent sublimation point $C$ and the lowest total pressure point. The point $V$s under four temperatures are deduced and fitted by equation

$$V(T) = [50 + \alpha \exp(\beta T)]100\%$$

(10)

where the fitting parameter $\alpha = 2.511 \times 10^{-6}$ and $\beta = 0.005635$, as shown in Fig. 3. Using Eq. (10), we can estimate the point $V$ at the growth temperature range (820–1000 K), adjacent to the experimental data. However, such fitted point $V$ in Eq. (10) is only a reference close to the point where the two partial pressure curves cross.

The fitted curve using Eq. (9) as a function of solute molar number $a$ (calculated from Eq. (6)) is shown in Fig. 4, where the Cd curve is fitted when Cd pressure is dominant and the Te curve is fitted when Te$_2$ pressure is dominant. The fitted curve is tolerable when the molar number $a$ is between 0 and $1 \times 10^{-4}$ under these four temperatures. The fitting parameters of Eq. (9) are then plotted as a function of temperature $T$, as shown in Fig. 5, where $H_0$ is fitted by Clausius–Clapeyron relation as a function of $T$ and others are fitted linearly.

The growth model for diffusion-limited transport is discussed previously [1] and the equations under steady state

$$J_{Cd} = \frac{D_{Cd}}{R} \ln \left(\frac{P_{Cd}(F_{sou}, T_{sou})}{P_{Cd}(F_{sub}, T_{sub})}\right)$$

$$J_{Te} = \frac{D_{Te}}{R} \ln \left(\frac{P_{Te}\(F_{sou}, T_{sou})}{P_{Te}\(F_{sub}, T_{sub})}\right)$$

$$J_{Cd} = 2J_{Te}$$

(11)

yield one equation and two unknowns which is the source material composition $F_{sou}$ and the substrate grown material composition $F_{sub}$. In Eq. (11), $J_{Cd}$ and $J_{Te}$ are the molar fluxes of Cd and Te$_2$ per unit area per unit time (mol m$^{-2}$ s$^{-1}$) respectively, $R$ is the ideal gas constant in unit of m$^3$ Pa K$^{-1}$ mol$^{-1}$, $T$ is the average temperature of the source and the substrate in unit of K, $D_{Cd}$ and $D_{Te}$ are the diffusivity coefficients of Cd and Te$_2$ respectively, in unit of m$^2$ s$^{-1}$ and $h$ is the spacing between the source and the substrate in unit of meter. When helium is used as the carrier gas, the system can be treated as a binary gas diffusion system of Cd/He or Te$_2$/He. The diffusivity coefficients of Cd and Te$_2$ atoms in the binary system are carefully derived in the
Fig. 4. Curve fittings of solute vapor pressure as a function of solute molar number in the solvent.

Fig. 5. Fitting parameters of Cd and Te\textsubscript{2} and their curve fitting as a function of temperature.
Stefan–Maxwell form [5]

\[ D_{ij} = \frac{3kT}{8\pi \sigma_{ij} \sigma_{iT}^2} \left( \frac{kT}{2\pi m_i m_j} \right)^{1/2}, \]

where the calculated \( D \) is in unit of \( m^2 s^{-1} \), \( k \) is the Boltzmann constant in unit of \( J K^{-1} \), \( \sigma_{ij} \) is the average collision diameter in unit of meter, \( \sigma_{iT} = \frac{1}{2}\sigma_i + \frac{1}{2}\sigma_T \), \( P_{\text{total}} \) is the total pressure in unit of Pascal and \( m \) is the molecular (atomic) mass in unit of kilograms. The collision diameters as a function of temperature can be calculated using [1]

\[ \sigma(T) = \sigma_{\text{in}} (1 + C/T)^{1/2}, \]

with coefficients used by Bube et al. [1]. To get correct dimension and magnitude, all the units have been carefully treated. On the source side, the solute molar numbers of \( \text{Cd} \) and \( \text{Te}_2 \) can be calculated from \( F_{\text{source}} \). On both the source and the substrate, the partial pressure of the dominant component can be calculated by Eq. (9) using the fitted parameters as a function of temperature, while the partial pressure of the other component can be calculated by Eq. (8). Thus the solute molar numbers of the grown material under lower temperatures can be calculated and then its composition can be determined.

### 2.3. Model results

The source material composition \( F_{\text{source}} \), the source temperature (\( T_{\text{source}} = 940 \) K) and the substrate temperature (\( T_{\text{sub}} = 800, 840 \) and \( 880 \) K) are assigned as input of Eq. (11). The background Helium pressure is 50 Torr and the distance between the source and the substrate is 4 mm. The calculated molar number shifts under different substrate temperatures are shown in Fig. 6, where the positive number indicates that the composition of the substrate material shifts towards more \text{Te}-rich compared to the source material. The molar number shift is equivalent to adding \( x \) moles of \( \text{Te} \) into 1 mol of the source material. Although the compositional shift is too small to measure, it may affect the crystal stoichiometry and significantly change the electrical property of the material. It is also clear that the diffusivity which is inversely proportional to the total pressure limits the flux of material transport. The calculated growth rate is shown in Fig. 8, assuming \( \alpha \) is unity. The maximum growth rate is achieved at the point \( V \) of that deposition temperature (\( P_{\text{Cd}} = 2P_{\text{Te}_2} \)). When \( P_{\text{Cd}} \) dominates, the growth rate is significantly limited. It is also suppressed gradually when \( P_{\text{Te}_2} \) is dominant.

The calculation of deposition rate pales in front of the experimental result in many aspects. First of all, experimentally, the sticking coefficient \( \alpha \) is undetectable. For small experimental setups, \( \alpha \) may also include the undetectable losses of the source material from the edges or carried away by the ambient gas. Second, by decreasing the helium background pressure to \( < \) 30 Torr, the calculated growth rate using diffusion model becomes unreasonably larger than the

![Fig. 6. The calculated grown material (substrate) molar number shift under three different substrate temperatures as a function of source material composition.](image6)

![Fig. 7. Calculated diffusivity of Cd and \( \text{Te}_2 \) during CSS under different substrate temperature as a function of source material composition.](image7)

![Fig. 8. Calculated growth rate as a function of source material composition under different substrate temperatures, assuming the sticking coefficient is unity.](image8)
experimental result, because the deposition mechanism is changing from diffusion limited to sublimation limited [2]. Third, the design of the CSS crucible can limit the deposition rate. For bigger CSS systems, the actual temperature on the surface of the substrate, which is meant to be controlled by the substrate heater (top heater), may be affected by the radiation heating from the source. As shown in Fig. 9, the thermal analysis diagram shows the total heat flow $Q_T$ from the bottom plate to top plate [1]. Ideally, there is a big thermal resistance ($R_3$ in Fig. 9) between the source and the substrate surfaces due to the physical gap between the source and substrate. In addition to heat transport by conduction and/or convection through the carrier gas ($R_1$), there is also a parallel radiative component from the source (shown as the extra path through $R_{rad}$). The radiation component limits the maximum of the temperature difference $\Delta T$ between $T_S$ and $T_g$, and thus limits the maximum deposition rate achievable for the system. Moreover, during dynamic fabrications with substrate transportation, there is an extra vacuum gap between the substrate and the top crucible surface, limiting the temperature difference $\Delta T$ between the source and the grown materials. In these cases, the actual deposition rate is not only affected by the sticking coefficient.

It must be pointed out that the system in the calculation is assumed to be in steady state with constant composition of the materials on the source and the substrate and with zero loss from edge leakage/oxidation. However, the system in reality is more complicated, resulting in more severe non-stoichiometric shift of grown material. First, in real CSS deposition crucibles, the source material is in the form of grains with limited mass. As predicted from Fig. 7, the composition of the source material will shift towards the composition at point $V$. Second, the oxygen induced into the system will consume Cd, making the source/substrate more Te-rich and increasing the deposition rate if the source material is initially stoichiometric. Third, materials will leak out from the edge of the crucible. Due to atomic mass difference, the diffusivity of Cd atoms is always bigger than that of Te$_2$ molecules, leading to severe non-stoichiometric loss of materials e.g. “Knudsen cell” model. In those cases, the stability of the CSS deposition can be affected in the long run.

At higher substrate temperatures, surface reactions will likely play a major role in growth. For example, at high substrate temperatures, neither Cd nor Te will stick unless they either react to form the less volatile CdTe phase. This is also why O$_2$ is sometimes added to the gas phase since oxides like CdO and TeO$_2$ are less volatile than Cd or Te and provide an additional path to forming CdTe. The solubility of Cd or Te in CdTe also plays a role in the growth. For example, a Cadmium molecule can dissolve in the existing solid-phase CdTe on the substrate before reacting with Tellurium until it is saturated. If the solid-phase CdTe is already saturated with Cd or Te atoms, the Cd or Te cannot stick unless they either react to form the less volatile CdTe phase.

3. Conclusion

Based on the experimental data of partial pressures of CdTe vapor phases and diffusion transport equations, the grown substrate material compositions are calculated as a function of the source material composition and other growth conditions. The solid phase Cd$_{1-x}$Te$_{1-x}$ compound in the source material under CSS deposition temperature is treated as a solid solution with $x$ mole of excess pure Te or Cd as solute and one mole of CdTe at composition point $V$ as solvent, at which point the partial pressures of Cd and Te$_2$ are 1:2 (stoichiometric). Assuming the vapor pressures of Cd and Te$_2$ can be calculated using the law of solid solution, $P_{Cd2/Te}$ = $P_{0}$($\delta H_{f} + a\delta H_{2}$) rounded the composition point $V$, the experimental partial pressure curves under higher temperatures (1073–1223 K) as a function of solute molar number $a$ are fitted. The coefficients $H_f$ under the CSS temperatures are calculated from extensions of the existing experimental data under higher temperatures. As a result, by putting the calculated partial pressures into the diffusion transport equations, the molar number shift of the grown CdTe thin film and the growth rate, as functions of the molar number of the source material, are determined.

It is shown that the composition of the grown CdTe from a more Te-rich source material than the composition at point $V$ will become more Te-rich. This shift may create more Cd vacancies and/or more Te interstitials. It is also shown that the composition of the grown CdTe from a more Cd-rich source material than the composition at point $V$ will become more Cd-rich, which may decrease the Cd vacancies and/or increase Cd interstitials and Te vacancies. The composition at point $V$ is almost the congruently-grown composition, which divides the two different composition shift directions. Additionally, larger temperature difference between the source and the substrate results in larger composition shifts. Lastly, the growth rate peaks at the composition point $V$ and it becomes severely suppressed at more Cd-rich compositions.

From the calculated results, it is discussed that in principle the CSS technology itself is reliable, because stable deposition can be achieved at the congruent-growth composition which is close to composition point $V$. However, in reality the stability of the CSS deposition will be affected in the long run, for example, by limited amount of source material, poorly-controlled reaction oxygen concentration, non-stoichiometric edge leaking of source materials or limited surface reactions.

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