PHYSICAL MODEL OF DEFECT FORMATION IN NON-STOICHIOMETRIC CADMIUM TELLURIDE

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ABSTRACT: In this work, we propose a physical model of defect formation in non-stoichiometric cadmium telluride (CdTe) by detailing the change of free energy for CdTe thin film under growth. The model explains the dependence of various intrinsic point defect densities in CdTe lattice on temperature, on Fermi level, and on vapor pressures of Cd and Te_2 during physical vapor deposition (PVD). The model also establishes a physical foundation for the experimentally observed relationship between the stoichiometry of CdTe films and the vapor pressures of Cd and Te_2 via the formation of various defects. The simulation results based on the model provide theoretical insights and practical guidance for experimentalists to fine tune the carrier concentration in CdTe thin films.

Keywords: CdTe, stoichiometry, carrier concentration, intrinsic defects, defect formation

1 INTRODUCTION

CdTe is one of the most widely used materials for low cost, high efficiency thin film photovoltaic (PV) applications. The intrinsic point defects of CdTe, such as vacancy, interstitial and antisite, play critical roles in the dopant and deep level concentrations. Thus, it is important to optimize the growth conditions of physical vapor deposition (PVD), either close space sublimation (CSS) or vapor transport deposition (VTD), so that the dopant concentration is high, and deep level density is low. The experimentally observed relationship between the stoichiometry of CdTe and the vapor pressures of Cd and Te_2 at various temperatures were published 20 years ago [1], which is illustrated in Fig. 1. There was no theoretical work to explain the relationship of the stoichiometry and the vapor phase pressures until recently, where Chin et al. assume that the non-stoichiometric CdTe thin film behaves as a solid solution [2]. By invoking the Henry's Law, they were able to give an interpretation of the experimental results. Yet, such an interpretation is phenomenological. There is no physical evidence that the non-stoichiometric CdTe polycrystalline thin film is indeed a solid solution.

Alternatively, there may exist a more fundamental correlation between the CdTe stoichiometry and the partial vapor pressures of Cd and Te_2 via the formation of various defects with different densities. Therefore, we use the data of formation energies of point defects in CdTe which were obtained by first-principles calculation at zero temperature [3], to develop a physical model of defect formation in non-stoichiometric CdTe. Unlike the theoretical work based on first-principles calculation, our model expresses the chemical potentials as a function of pressure and temperature for practical emphasis. Our model establishes a physical foundation to explain the dependence of various intrinsic defect densities on temperature, on Fermi level, and on vapor pressures of Cd and Te_2 during physical vapor deposition.
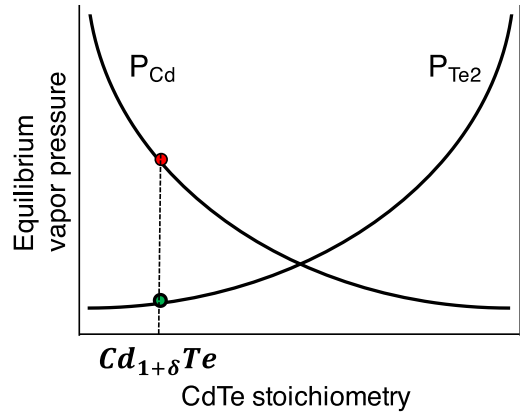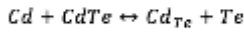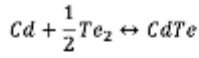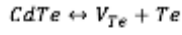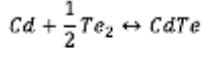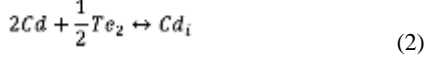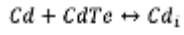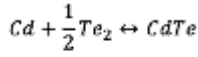

Figure 1: Illustration of the experimentally observed relationship between the stoichiometry of CdTe and the partial vapor pressures of Cd and Te_2.

2 RELATIONSHIP OF CDTE STOICHIOMETRY AND THE POINT DEFECT DENSITIES

As experimentally observed, there are two types of non-stoichiometric CdTe thin films: Cd-rich or Te-deficient, and Cd-deficient or Te-rich. Assuming the deviation from perfect stoichiometric CdTe crystal is small, the two types of slightly non-stoichiometric CdTe can be expressed as

$$Cd_{1+\delta}Te \sim CdTe_{1-\delta} \text{ and } Cd_{1-\delta}Te \sim Cd \qquad (1)$$

respectively.

For Cd-rich CdTe, the dominant point defects are tellurium vacancy V_{Te}, cadmium interstitial Cd_i, and cadmium on tellurium antisite Cd_{Te}, with densities of $\delta_{V_{Te}}$, δ_{Cd_i}, and $\delta_{Cd_{Te}}$, respectively. The formation of these three point defects can be formulated as:

$$Cd + \frac{1}{2}Te_2 \leftrightarrow CdTe$$

$$Cd + CdTe \leftrightarrow Cd_i$$

$$\overline{2Cd + \frac{1}{2}Te_2 \leftrightarrow Cd_i} \tag{2}$$

$$Cd + \frac{1}{2}Te_2 \leftrightarrow CdTe$$

$$CdTe \leftrightarrow V_{Te} + Te$$

$$\overline{Cd \leftrightarrow V_{Te}} \tag{3}$$

$$Cd + \frac{1}{2}Te_2 \leftrightarrow CdTe$$

$$Cd + CdTe \leftrightarrow Cd_{Te} + Te$$

$$\overline{2Cd \leftrightarrow Cd_{Te}} \tag{4}$$

where CdTe is a primitive unit cell of CdTe in the perfect CdTe crystal. The non-stoichiometry index δ of Cd-rich CdTe due to its point defects V_{Te}, Cd_i and Cd_{Te} should satisfy the relationship:

$$\delta_{V_{Te}} + \delta_{Cd_i} + 2\delta_{Cd_{Te}} = \delta \tag{5}$$
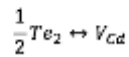
Similarly, for Te-rich CdTe, the dominant point defects are cadmium vacancy V_{Cd}, tellurium interstitial Te_i, and tellurium on cadmium antisite Te_{Cd}, with densities of $\delta_{V_{Cd}}$, δ_{Te_i} and $\delta_{Te_{Cd}}$, respectively. The formation of these three point defects can be formulated as:
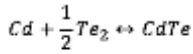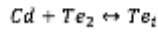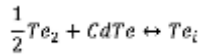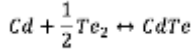
$$Cd + \frac{1}{2}Te_2 \leftrightarrow CdTe$$

$$\frac{1}{2}Te_2 + CdTe \leftrightarrow Te_i$$

$$\overline{Cd + Te_2 \leftrightarrow Te_i} \tag{6}$$

$$Cd + \frac{1}{2}Te_2 \leftrightarrow CdTe$$

$$CdTe \leftrightarrow V_{Cd} + Cd$$

$$\overline{\frac{1}{2}Te_2 \leftrightarrow V_{Cd}} \tag{7}$$

$$Cd + \frac{1}{2}Te_2 \leftrightarrow CdTe$$

$$\frac{1}{2}Te_2 + CdTe \leftrightarrow Te_{Cd} + Cd$$

$$\overline{Te_2 \leftrightarrow Te_{Cd}} \tag{8}$$
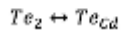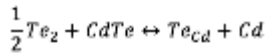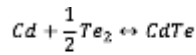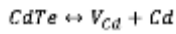
The non-stoichiometry index δ of Te-rich CdTe due to its point defects V_{Cd}, Te_i and Te_{Cd} should satisfy a similar relationship:

$$\delta_{V_{Cd}} + \delta_{Te_i} + 2\delta_{Te_{Cd}} = \delta \tag{9}$$

3 DEPENDENCE OF INTRINSIC DEFECTS DENSITIES ON TEMPERATURE, ON FERMI LEVEL, AND ON VAPOR PRESSURES OF CD AND TE2 UNDER PVD CONDITION

From equations (2) to (4), the free energy of point defect formation in Cd-rich CdTe can be expressed as:

$$2\mu_{Cd} + \frac{1}{2}\mu_{Te_2} \leftrightarrow G_{Cd_i} \tag{10}$$

$$\mu_{Cd} \leftrightarrow G_{V_{Te}} \tag{11}$$

$$2\mu_{Cd} \leftrightarrow G_{Cd_{Te}} \tag{12}$$

We assume that at the growth temperature T of CdTe thin film, thermodynamic equilibrium is reached in the solid-vapor system. By considering the energy change due to vapor heat capacity, the energy change due to pressure, the energy change due to intermixing, the change of formation energy as a function of Fermi level E_f, and the change of configurational entropy due to defect formation, the three equilibrium conditions described in terms of the change of free energy can be detailed as:

$$\int_0^T 2C_p^{Cd}dT + \int_0^T \frac{1}{2}C_p^{Te_2}dT + 2kTln\left(\frac{P_{Cd}}{P_o}\right)$$
$$+ \frac{1}{2}kTln\left(\frac{P_{Te_2}}{P_o}\right) + 2kTln\left(\frac{2}{2.5}\right) + \frac{1}{2}kTln\left(\frac{0.5}{2.5}\right)$$
$$= \Delta H_{Cd_i} + qE_f + \int_0^T C_p^{Cd_i}dT + T\left[kln(\delta_{Cd_i})\right] \tag{13}$$

$$\int_0^T C_p^{Cd}dT + kTln\left(\frac{P_{Cd}}{P_o}\right)$$
$$= \Delta H_{V_{Te}} + qE_f + \int_0^T C_p^{V_{Te}}dT + T\left[kln(\delta_{V_{Te}})\right] \tag{14}$$

$$\int_0^T 2C_p^{Cd}dT + 2kTln\left(\frac{P_{Cd}}{P_o}\right)$$
$$= \Delta H_{Cd_{Te}} + qE_f + \int_0^T C_p^{Cd_{Te}}dT + T\left[kln(\delta_{Cd_{Te}})\right] \tag{15}$$

where the formation energies of the three dominant defects in Cd-rich CdTe are ΔH_{Cd_i}, $\Delta H_{V_{Te}}$ and $\Delta H_{Cd_{Te}}$, respectively, with $\Delta H_{CdTe} = 0$. The formation energies of point defects have been calculated at 0 K using first-principles methods [3].

Considering Cd and Te_2 vapors as monoatomic and diatomic ideal gas, respectively, $C_p^{Cd} = \left(\frac{3}{2} + 1\right)k$, $C_p^{Te_2} = \left(\frac{7}{2} + 1\right)k$, where k is the Boltzmann constant. Since heat capacity of point defect is quite small (~ 0.1 eV) relative to the formation energies of various defects that are on the order of a few eV, the term of point defect heat capacity can be neglected in our calculations. Note that the degeneracy of a point defect is the inverse of the defect density.

Assuming CdTe solid-vapor system is at equilibrium, we have the equation of chemical reaction equilibrium:

$$P_{Cd}\sqrt{P_{Te2}} = exp\left[\frac{-\Delta G_{CdTe}(T)}{RT}\right] \tag{16}$$

Consequently, equations (13) to (15) can be simplified into:

$$6 - \frac{\Delta H_{Cd_i} + qE_f + \Delta G_{CdTe}(T)}{kT} + \ln P_{Cd} = \ln\delta_{Cd_i} \quad (17)$$

$$\frac{5}{2} - \frac{\Delta H_{V_{Te}} + qE_f}{kT} + \ln P_{Cd} = \ln\delta_{V_{Te}} \quad (18)$$

$$5 - \frac{\Delta H_{Cd_{Te}} + qE_f}{kT} + 2\ln P_{Cd} = \ln\delta_{Cd_{Te}} \quad (19)$$

Similarly, for the three dominant point defects in Te-rich CdTe, their equilibrium conditions of defect formation described in terms of the change of free energy can be detailed as:

$$\int_0^T (C_p^{Cd} + C_p^{Te_2})dT + kT\ln\left(\frac{P_{Cd}P_{Te_2}}{P_o^2}\right) - kT\ln 4$$
$$= \Delta H_{Te_i} - qE_f + \int_0^T C_p^{Te_i}dT + T[k\ln(\delta_{Te_i})] \quad (20)$$

$$\int_0^T \frac{1}{2}C_p^{Te_2}dT + \frac{1}{2}kT\ln\left(\frac{P_{Te_2}}{P_o}\right)$$
$$= \Delta H_{V_{Cd}} - qE_f + \int_0^T C_p^{V_{Cd}}dT + T[k\ln(\delta_{V_{Cd}})] \quad (21)$$

$$\int_0^T C_p^{Te_2}dT + kT\ln\left(\frac{P_{Te_2}}{P_o}\right)$$
$$= \Delta H_{Te_{Cd}} - qE_f + \int_0^T C_p^{Te_{Cd}}dT + T[k\ln(\delta_{Te_{Cd}})] \quad (22)$$

where the formation energies are ΔH_{Te_i}, $\Delta H_{V_{Cd}}$ and $\Delta H_{Te_{Cd}}$, respectively. With the equation of chemical reaction equilibrium, equations (20) to (22) can be simplified into:

$$7 - 2\ln 2 - \frac{\Delta H_{Te_i} - qE_f + \Delta G_{CdTe}(T)}{kT} + \frac{1}{2}\ln P_{Te_2}$$
$$= \ln\delta_{Te_i} \quad (23)$$

$$\frac{9}{4} - \frac{\Delta H_{V_{Cd}} - qE_f}{kT} + \frac{1}{2}\ln P_{Te_2} = \ln\delta_{V_{Cd}} \quad (24)$$

$$\frac{9}{2} - \frac{\Delta H_{Te_{Cd}} - qE_f}{kT} + \ln P_{Te_2} = \ln\delta_{Te_{Cd}} \quad (25)$$
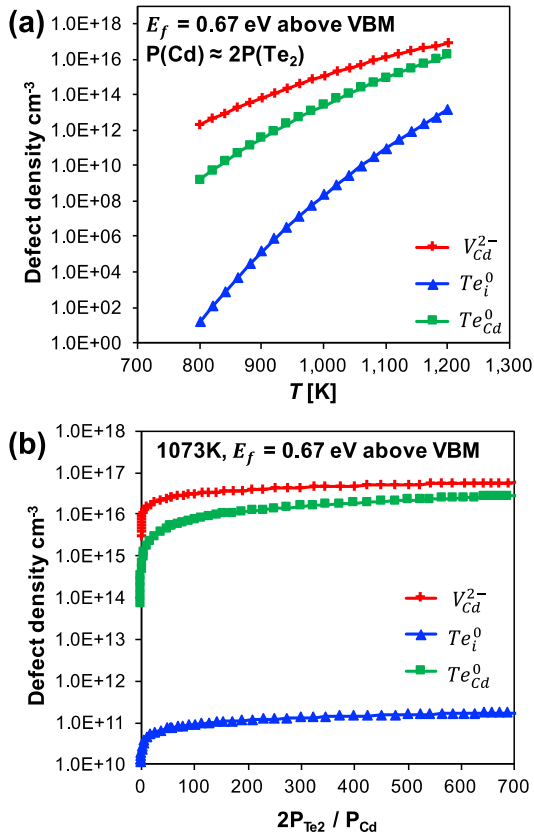
4   MODELING RESULTS AND DISCUSSION

From the equations (17) to (19), the point defect densities in Cd-rich CdTe depend on the growth temperature and on the vapor pressure of Cd. As the formation energies of defects change with the Fermi level E_f, the point defect densities also depend on doping that could change the E_f of CdTe. To demonstrate the dependence of defect densities on growth temperature T, we took equations (17) to (19) to calculate the defect densities as a function of increasing temperature T, while keeping E_f and the ratio of P_{Cd}/P_{Te_2} fixed ($E_f = 0.24$ eV below the conduction band minimum (CBM) and $P_{Cd} \approx 2P_{Te_2}$). DFT study has previously shown that in Cd-rich CdTe Fermi level E_f will be pinned around 0.24 eV below CBM, due to self-compensation, no matter how high the

growth temperature is [4]. To demonstrate the dependence on vapor pressure, we took equations (17) to (19) to calculate the defect densities as a function of increasing P_{Cd}/P_{Te_2}, while keeping E_f and the growth temperature T fixed ($E_f = 0.24$ eV below the CBM and $T = 1073K$). The results of modeling are shown in Figure 2. It should be mentioned that the free energy of point defect does not depend on the electric charge of the point defect.
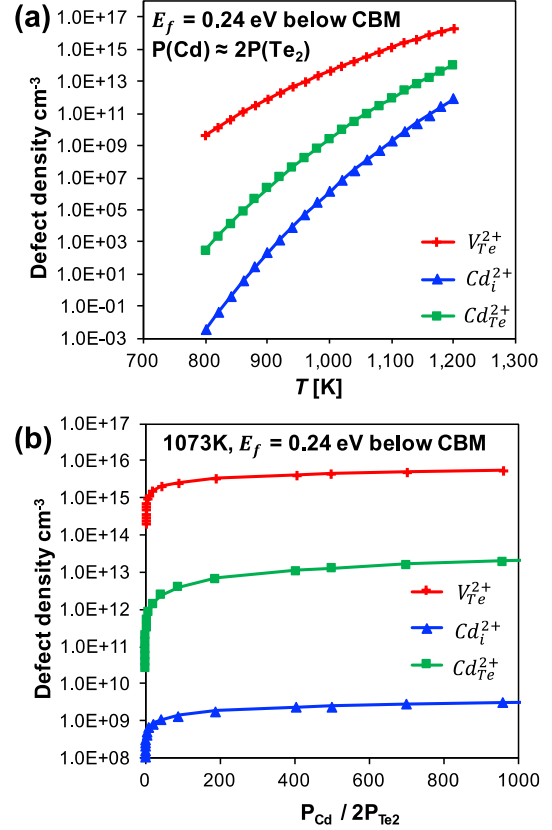
Figure 2: Modeling results of intrinsic point defect density in Cd-rich CdTe as a function of (a) growth temperature, and (b) vapor pressure ratio of P_{Cd}/P_{Te_2}.

From the equations (23) to (25), the point defect densities in Te-rich CdTe instead depend on the vapor pressure of Te₂, different from that in Cd-rich CdTe. To demonstrate the dependence of defect densities on growth temperature T, we took equations (23) to (25) to calculate the defect densities as a function of increasing temperature T, while keeping E_f and the ratio of P_{Te_2}/P_{Cd} fixed ($E_f = 0.67$ eV above the valance band maximum (VBM) and $P_{Cd} \approx 2P_{Te_2}$). DFT study has previously shown that in Te-rich CdTe Fermi level E_f will be pinned around 0.67 eV above VBM, which is the lowest E_f achievable for p-type CdTe under thermodynamic equilibrium growth conditions [4]. To demonstrate the dependence on vapor pressure, we took equations (23) to (25) to calculate the defect densities as a function of increasing P_{Te_2}/P_{Cd}, while keeping E_f and the growth temperature T fixed ($E_f = 0.67$ eV above the VBM and $T = 1073K$). The results of modeling are shown in Figure 3.

(a)

E_f = 0.67 eV above VBM
P(Cd) ≈ 2P(Te₂)

Defect density cm⁻³ (y-axis: 1.0E+00 to 1.0E+18)

T [K] (x-axis: 700 to 1,300)

V_{Cd}^{2-}
Te_i^0
Te_{Cd}^0

(b)

1073K, E_f = 0.67 eV above VBM

Defect density cm⁻³ (y-axis: 1.0E+10 to 1.0E+18)

2P$_{Te2}$ / P$_{Cd}$ (x-axis: 0 to 700)

V_{Cd}^{2-}
Te_i^0
Te_{Cd}^0

Figure 3: Modeling results of intrinsic point defect densities in Te-rich CdTe as a function of (a) growth temperature, and (b) vapor pressure ratio of P_{Te_2}/P_{Cd}.

As shown in Fig. 2(a) and Fig. 3(a), in either Cd-rich or Te-rich CdTe, all point defect densities increase with higher growth temperature. While the vacancies, i. V_{Te}. and V_{Cd}, are beneficial in Cd-rich and Te-rich CdTe lattice respectively for higher carrier concentration, the interstitial and antisite are usually harmful (deep level defects) compensating the doping efficiencies of vacancy-related defects. As the densities of vacancies are usually one or more orders of magnitude higher than the densities of the other two defects at a given temperature, higher growth temperature seems to be more beneficial for CdTe thin film grown under PVD condition to reach high carrier concentration. After growth, the CdTe thin film is quenched to room temperature. The defect densities formed during growth are thus kept.

As shown in Fig. 2(b) and Fig. 3(b), higher vapor pressure of Cd during PVD increases the point defect densities in Cd-rich CdTe thin film, and higher vapor pressure of Te₂ during PVD increases the point defect densities in Te-rich CdTe thin film. However, based on the relative densities of beneficial defects (vacancies) vs. harmful defects (interstitial and antisite), the vapor pressure dependence under Cd-rich condition is more useful than that under Te-rich condition to fine tune the carrier concentration in CdTe thin films.

It is worth mentioning that as the CdTe thin film growth temperature is around 500 ~ 700° C, the actual bandgap of CdTe during growth may be significantly smaller comparing to the value at room temperature. Such decrease in bandgap at high temperature has not been considered in our modeling. Like the studies using DFT calculation, our modeling still considered standard bandgap value of CdTe, i.e. 1.5 eV. Future experimental or theoretical studies may be needed to investigate the proper bandgap value of CdTe at such high temperatures.

5 CONCLUSION

The non-stoichiometric growth of CdTe thin film is due to the defect formation that determined by, not only the formation energy of the defects, but also the growth temperature and the vapor pressures of Cd and Te₂. In this work, we report a new physical model of defect formation that explains the dependence of intrinsic point defect densities on temperature, on Fermi level, and on vapor pressures of Cd and Te₂ during physical vapor deposition. The proposed model enables the experimentalists to fine tune the growth condition, so that the carrier concentration is high, and deep level density is low.

6 REFERENCES

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