CdTe Growth Model by Close Spaced Sublimation

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Abstract—Close spaced sublimation (CSS) has attractive features for high-rate deposition of CdS/CdTe thin film solar modules. It is necessary to have a solid growth model to explain their growth. In past 20 years, there are several growth models which are conflict each other. In this paper, a growth model was developed for CdTe deposition. The model can explain the effect of source and substrate temperature, ambient gas pressure and the separation between source and substrate on the growth rate of CdTe by CSS.

Index Terms — CSS, CdS/CdTe, growth model

I. INTRODUCTION

Cadmium telluride (CdTe) thin film is the most promising solar cells because of its long term stable performance, easy scale-up, high absorption coefficient and optimum band gap. In 2015, a new world record conversion efficiency 21.5% for CdTe solar was announced by First Solar. CdTe deposited by CSS technique are expected to have the highest deposition rate and were successfully used in industry. So it is very important to build a growth model to explain and predict the growth rate of the CSS. There are several growth models in past thirty years. Jose’s Model [1] explained the idea gas and stoichiometry CdTe growth model and assumed the pressure of Cd is twice of the pressure of Te2 which is conflict with the paper of greenberg’s [2]. Bube’s model [3] is based on the Fick’s law and assumed the subject pressure is negligible. He simplified the 5 unknown and 4 equations to 3 unknown and 3 equations. He successfully solve growth rate, but his model is not accurate. Chin’s Model [4] successfully solve bube’s model by adding one more equations according to Henry’s law. Chin’s model can be used to solve non-stoichiometry CdTe growth. However his model is too complicated and not easy to understand. Guogen’s Model [5] use the experimental data and bube’s mode to build a half theory and half experimental model. It is simple and easy to understand. In this paper, we will introduce another model which is more accurate than bube’s model.

II. Experimental

We used the CBD to deposit 80nm CdS on 4*6 inch TCO glass. The CdS substrate is then loaded in the deposition chamber as shown in. Fig.1 and Fig. 2.

Fig. 1. CSS deposition system

Fig. 2. Schematic diagram of CSS deposition chamber

The CdTe deposition is the reversible dissociation of CdTe at high temperatures. The CdTe deposition chemical process equation by CSS is below:

A. \[ CdTe(s) \rightarrow Cd(g) + \frac{1}{2} Te_2(g) \]

The equilibrium constant is:

\[ K_{CdTe}(T_{Sour}) = P_{Cd}(0)P_{Te_2}(0)^{1/2} \]

where \( P_{Cd}(0) \) and \( P_{Te_2}(0) \) are the equilibrium pressure of Cd and Te2 at the temperature of source \( T_{Sour} \). The equilibrium constant can be calculated from the expression given by deLargy et al.
\[
K_{CdTe}(T_{Sub}) = P_{Cd}(0)P_{Te2}(0)^{1/2} = \exp\left[-\frac{\Delta G_{CdTe(T_{Sub})}}{RT_{Sub}}\right] \quad (1)
\]

\[
\Delta G_{CdTe(T_{Sub})} = 68.64 - 44.94 \times 10^{-3} T \text{ kcal/mol}
\]

B. Diffusion Model

If the mean free path of Cd atoms and Te₂ molecules is longer than the space between the source and substrate ( \( \lambda > h \)), then it is diffusion model.

In the diffusion model, the growth rate can be calculated by Fick’s law.

\[
J_{cd} = \frac{D_{cd,j}}{kT_{ave}^3} (P_{Cd}(0) - P_{Cd}(h)) \quad (5)
\]

Where \( k \) is Boltzmann’s constant(J/K), \( T_{ave} \) is the average temperature between source and substrate, \( D_{cd,j} \) is the binary coefficient of diffusion of cadmium diffusing into inert gas \( j \) (m²/s); This coefficient will be calculated using the Stefan–Boltzmann model given as

\[
D_{Cd,j} = \frac{(NA(KT_{ave}/\pi)^3 * (1/m_{Cd} + 1/m_j))^{1/2}}{3(NAKTm_{Cd}m_j)^{1/2}} \quad (6)
\]

where \( m_{Cd} \) and \( m_j \) are the molar masses of cadmium and helium (kg/mol), \( P_{Cd,ave} \) is the vapor pressure(Pa) of Cd evaluated at the average of the substrate and source temperatures \( T_{ave} \) (K), \( P_i \) is the chamber pressure(Pa), \( NA \) is Avogadro’s number, \( K \) is Boltzmann constant, and \( \sigma_{Cd,j} \) is the average molecular diameter.

\[
\sigma_{Cd,j} = \frac{\sigma_{Cd} + \sigma_j}{2}
\]

\[\text{Fig. 3. The diagram of CSS deposition model}\]

η is the deposition efficiency. It is an empirical constant that adjust the model’s output to match experimental data. So the diffusion model can be summarized as 6 equations with 6 unknowns: \( P_{Cd}(0), P_{Te2}(0), P_{Cd}(h), P_{Te2}(h) \)

\[
J = \partial h
\]

\[
K_{CdTe}(T_{Sub}) = P_{Cd}(0)P_{Te2}(0)^{1/2} = \exp\left[-\frac{\Delta G_{CdTe(T_{Sub})}}{RT_{Sub}}\right] \quad (1)
\]

\[
K_{CdTe}(T_{Sub}) = P_{Cd}(h)P_{Te2}(h)^{1/2} = \exp\left[-\frac{\Delta G_{CdTe(T_{Sub})}}{RT_{Sub}}\right] \quad (2)
\]

\[
P_{Cd}(0) = 3P_{Te2}(0) \quad (3)
\]

A. Sublimation model

If the mean free path of Cd atoms and Te₂ molecules is longer than the space between the source and substrate ( \( \lambda > h \)), then it is sublimation model.

\[
\hat{\lambda} = \frac{KT}{\sqrt{2\pi d^2}} \quad (3)
\]

where \( k \) is Boltzmann’s constant, \( P \) is the pressure (Pa), \( T \) is the source temperature (K) and \( d \) is the molecular diameter of Cd and Te₂.

In the sublimation model, the growth rate is proportional to the equilibrium vapor pressure difference between the source and the substrate.

\[
G_{Sub}(m/s) = \frac{\alpha \beta (P_{sou}T_{sou} - P_{sub}T_{sub})N_A m_j}{\sqrt{\pi m_j RT_{ave}}} \quad (4)
\]

where \( \alpha \) and \( \beta \) are coefficients with values between 0 and 1; \( P_{sou} \) and \( P_{sub} \) are the vapor pressure (Pa) of i in the source and substrate; \( m_i \) represents the molar mass of the source material(kg/mol); \( R \) is the universal gas constant(J/(kgmol)); \( T_{sou}, T_{sub} \) and \( T_{ave} \) are the source, substrate, and average temperatures, respectively(K); \( NA \) is Avogadro’s number; and \( \rho_j \) represents the density of the substance evaporated(kg/m³).
After we simplify the equation, we can get three equations and 3 unknowns. \( P_{cd}(0) = \frac{1}{\partial^2} \frac{1}{\partial^2} \frac{1}{\partial^2} P_{cd}(h) \)

\[
\frac{1}{\partial^2} P_{cd}(0)^2 = \exp\left[ -\frac{\Delta G_{\text{CdTe}}(T_{\text{sub}})}{RT_{\text{sou}}} \right]
\]

\[
\frac{1}{\partial^2} P_{cd}(h)^2 = \exp\left[ -\frac{\Delta G_{\text{CdTe}}(T_{\text{sub}})}{RT_{\text{sub}}} \right]
\]

\[
\partial = \frac{D_{\text{Te},j}}{D_{cd,j}}
\]

After the calculation, we get \( \partial = 1.05 \) at \( T_{\text{sub}} = 600^\circ \text{C} \); \( T_{\text{sou}} = 640^\circ \text{C} \);

The growth rate \( (\text{um/mim}) \) can be calculate from the material flux by

\[
G(\text{um/min}) = \alpha J_{cd} \frac{M_{\text{CdTe}}}{\rho_{\text{CdTe}}} \times 60 \times 10^6
\]

Where the coefficient \( \alpha \) is sticking coefficient. The fitting parameter value \( \alpha = 0.36[6] \), \( M_{\text{CdTe}} \) is molar mass in Kg/mol and \( \rho_{\text{CdTe}} \) is the density in Kg/m³.

At the \( T_{\text{sub}} = 600^\circ \text{C} \); \( T_{\text{sou}} = 640^\circ \text{C} \); \( h = 2 \text{mm} \), we calculate the deposition rate is 4.02um/min. It is very close to the experiment data of 4.33um/min. Table 1 shows the deposition rate for different substrate temperature at \( T_{\text{sou}} = 640^\circ \text{C} \). Table 2 shows the deposition rate and \( \partial \) for different source temperature at \( T_{\text{sub}} = 400^\circ \text{C} \).

**Figure 4** shows that the growth rate almost kept the same with the increase of \( T_{\text{sub}} \) when the \( T_{\text{sub}} \) is below to 550°C. The growth rate decrease greatly with the increase of \( T_{\text{sub}} \) when the \( T_{\text{sub}} \) is above to 550°C. It is because of the resublimation of CdTe on the substrate.

**Figure 5** compare the diffusion model with the former model [5] and the experimental data. The diffusion model is very accurate.

**Table 1**

<table>
<thead>
<tr>
<th>( T_{\text{sub}} ) (°C)</th>
<th>400</th>
<th>410</th>
<th>420</th>
<th>430</th>
<th>440</th>
<th>450</th>
<th>460</th>
<th>470</th>
<th>480</th>
<th>490</th>
<th>500</th>
<th>510</th>
<th>520</th>
</tr>
</thead>
<tbody>
<tr>
<td>G (um/min)</td>
<td>5</td>
<td>5.05</td>
<td>5.10</td>
<td>5.14</td>
<td>5.19</td>
<td>5.23</td>
<td>5.28</td>
<td>5.32</td>
<td>5.36</td>
<td>5.39</td>
<td>5.42</td>
<td>5.44</td>
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<table>
<thead>
<tr>
<th>( T_{\text{sub}} ) (°C)</th>
<th>530</th>
<th>540</th>
<th>550</th>
<th>560</th>
<th>570</th>
<th>580</th>
<th>590</th>
<th>600</th>
<th>610</th>
<th>620</th>
<th>630</th>
<th>640</th>
</tr>
</thead>
<tbody>
<tr>
<td>G (um/min)</td>
<td>5.43</td>
<td>5.40</td>
<td>5.33</td>
<td>5.22</td>
<td>5.06</td>
<td>4.82</td>
<td>4.48</td>
<td>4.02</td>
<td>3.39</td>
<td>2.55</td>
<td>1.44</td>
<td>0</td>
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</table>

**Table 2**

<table>
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<th>( T_{\text{sou}} ) (°C)</th>
<th>400</th>
<th>410</th>
<th>420</th>
<th>430</th>
<th>440</th>
<th>450</th>
<th>460</th>
<th>470</th>
<th>480</th>
<th>490</th>
<th>500</th>
<th>510</th>
<th>520</th>
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<tbody>
<tr>
<td>( \partial )</td>
<td>2</td>
<td>1.071</td>
<td>1.07</td>
<td>1.069</td>
<td>1.068</td>
<td>1.067</td>
<td>1.067</td>
<td>1.065</td>
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<td>1.062</td>
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</tr>
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</table>

**Figure 4.** The growth rate at different substrate temperature

**Figure 5.** The growth rate compare with experimental data
<table>
<thead>
<tr>
<th>G(um/min)</th>
<th>0</th>
<th>0.0003</th>
<th>0.0009</th>
<th>0.0018</th>
<th>0.0033</th>
<th>0.0055</th>
<th>0.0089</th>
<th>0.0139</th>
<th>0.0215</th>
<th>0.0325</th>
<th>0.0486</th>
<th>0.072</th>
<th>0.104</th>
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<tbody>
<tr>
<td>Tsub (°C)</td>
<td>530</td>
<td>540</td>
<td>550</td>
<td>560</td>
<td>570</td>
<td>580</td>
<td>590</td>
<td>600</td>
<td>610</td>
<td>620</td>
<td>630</td>
<td>640</td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>1.058</td>
<td>1.057</td>
<td>1.056</td>
<td>1.055</td>
<td>1.054</td>
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<td>1.048</td>
<td>1.047</td>
<td></td>
</tr>
<tr>
<td>G(um/min)</td>
<td>0.151</td>
<td>0.216</td>
<td>0.306</td>
<td>0.43</td>
<td>0.6</td>
<td>0.83</td>
<td>1.138</td>
<td>1.551</td>
<td>2.1</td>
<td>2.82</td>
<td>3.768</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6 shows that the ratio $\delta$ decreases with the increase of the $T_{sou}$. When $T_{sou}$ is between 400°C-500°C, the growth rate is almost zero, because CdTe evaporate very slowly. After 500°C, CdTe evaporate faster and the growth rate increase fast.

Figure 7 shows that the growth rate increases with the increase of $T_{sou}$. When $T_{sou}$ is between 400°C-500°C, the growth rate is almost zero, because CdTe evaporate very slowly. After 500°C, CdTe evaporate faster and the growth rate increase fast.

**VI. Conclusion**

In this paper, we summarized the former growth model and introduce the ratio $\delta$ to present a new growth models for CdTe deposition by CSS. The model is very accurate and can guide the experimental work very well.

**References**