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-stochiometry CdTe growth. However his model is too complicated and not easy to understand. Guogen's Model [5] use the experimental data and bube's modle 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

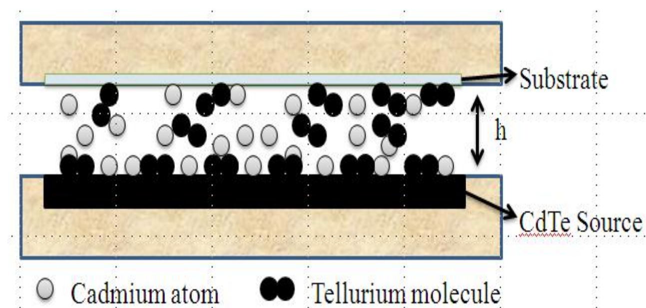

Fig. 2. Schematic diagram of CSS deposition chamber

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:

$$\mathrm{K}_{CdTe}(T_{Sou}) = P_{Cd}(0) P_{Te_2}(0)^{1/2}$$

where $P_{cd}(0)$ and $P_{Te2}(0)$ are the equilibrium pressure of Cd and Te_2 at the temperature of source T_{sou}. The equilibrium constant can be calculated from the expression given by deLargy et al.

$$K_{CdTe}(T_{Sou}) = P_{Cd}(0)P_{Te_2}(0)^{1/2} = \exp[\frac{-\triangle G_{CdTe(T_{Sou})}}{RT_{Sou}}] \quad (1)$$

$$\triangle G_{CdTe(T_{Sub})} = 68.64 - 44.94\times10^{-3}\mathrm{T\ kcal/mol}$$

B. $$Cd(g) + \frac{1}{2}Te_2(g) \rightarrow CdTe(s)$$

In the substrate, the Cd and Te_2 combines into CdTe at substrate temperature T_{sub}. The equilibrium constant is:

$$K_{CdTe}(T_{Sub}) = P_{Cd}(h)P_{Te_2}(h)^{1/2}$$

where $P_{cd}(h)$ and $P_{Te2}(h)$ are the equilibrium pressure of Cd and Te_2 at the temperature of substrate T_{sub}. The equilibrium constant is:

$$K_{CdTe}(T_{Sub}) = P_{Cd}(h)P_{Te_2}(h)^{1/2} = \exp[\frac{-\triangle G_{CdTe(T_{Sub})}}{RT_{Sub}}] \quad (2)$$

III, GROWTH MODEL

The growth model of CdTe is very complicated. To simplify the growth model, we just consider the situation of steady state, stochiometrical CdTe deposition. The growth rate depends on several interrelated parameters: the space between the source and the substrate, the temperatures of the source Tso and the substrate Tsub, and the pressure, temperature and composition of gases in the deposition chamber. According to different situation, we classify the growth model into two parts:

A. Sublimation model

If the mean free path of Cd atoms and Te_2 molecules is longer than the space between the source and substrate (λ >h), then it is sublimation model.

$$\lambda = \frac{KT}{\sqrt{2}\pi d^2 P} \quad (3)$$

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 Te_2.

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

$$G_{Subi}(m/s) = \frac{\alpha\beta(P^i_{\mathrm{sou}}T_{\mathrm{sou}} \text{-} P^i_{\mathrm{sub}}T_{\mathrm{sub}})N_A}{\sqrt{\pi m_i RT_{av}}}(\frac{m_i}{\rho_i}) \quad (4)$$

where α and β are coefficients with values between 0 and1; P^i_{sou} and P^i_{sub} are the vapor pressure (Pa) of i in the source and substrate; mi represents the molar mass of the source material(kg/mol); R is the universal gas constant(J/(kgmol)); T_{sou}, T_{sub}, and T_{av} are the source, substrate, and average temperatures, respectively(K); NA is Avogadro's number; and ρ_i represents the density of the substance evaporated(kg/m3).

B. Diffusion model

If the mean free path of Cd atoms and Te_2 molecules is longer than the space between the source and substrate (λ <h), then it is diffusion model.

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

$$J_{cd} = \frac{D_{cd,j}}{khT_{ave}}(P_{Cd}(0) - P_{Cd}(h)) \quad (5)$$

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

$$D_{Cd,j} = \frac{(NA(KT_{av}/\pi)^3 * (1/m_{Cd} + 1/m_j))^{1/2}}{3(P_{Cd,av} + P_j)\sigma^2_{Cd,j}} \quad (6)$$

where m_{Cd} and m_j are the molar masses of cadmium and helium (kg/mol), $P_{Cd,av}$ is the vapor pressure(Pa) of Cd evaluated at the average of the substrate and source temperatures T_{av} (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.

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

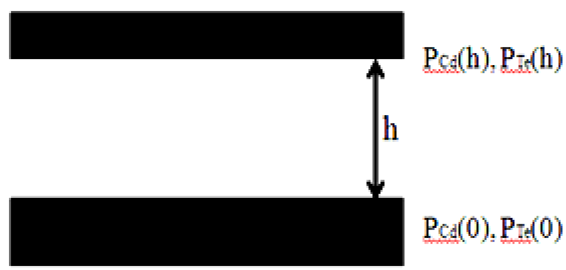

Fig. 3. The diagram of CSS deposition model

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 unknown: $P_{Cd}(0)$ $P_{Te_2}(0)$ $P_{Cd}(h)P_{Te_2}(h)$

J ∂

$$K_{CdTe}(T_{Sou}) = P_{Cd}(0)P_{Te_2}(0)^{1/2} = \exp[\frac{-\triangle G_{CdTe(T_{Sou})}}{RT_{Sou}}] \quad (1)$$

$$K_{CdTe}(T_{Sub}) = P_{Cd}(h)P_{Te_2}(h)^{1/2} = \exp[\frac{-\triangle G_{CdTe(T_{Sub})}}{RT_{Sub}}] \quad (2)$$

$$P_{Cd}(0) = \partial P_{Te_2}(0) \quad (3)$$

$$P_{Cd}(h) = \partial P_{Te_2}(h) \qquad (4)$$

$$J_{cd} = \frac{D_{cd,j}}{khT_{ave}}(P_{Cd}(0) - P_{Cd}(\mathrm{h})) = \mathrm{J} \qquad (5)$$

$$J_{Te_2} = \frac{D_{Te_2,j}}{khT_{ave}}(P_{Te_2}(0) - P_{Te_2}(\mathrm{h})) = \frac{1}{2}J \qquad (6)$$

After we simplify the equation, we can get three equations and 3 unknown. $P_{Cd}(0)$ $P_{Cd}(h)$ ∂

$$\frac{1}{\partial^{\frac{1}{2}}} P_{Cd}(0)^{\frac{3}{2}} = \exp[\frac{-\Delta G_{CdTe(T_{Sou})}}{RT_{Sou}}] \qquad (1)$$

$$\frac{1}{\partial^{\frac{1}{2}}} P_{Cd}(h)^{\frac{3}{2}} = \exp[\frac{-\Delta G_{CdTe(T_{Sub})}}{RT_{Sub}}] \qquad (2)$$

$$\partial = 2\frac{D_{Te_2,j}}{D_{cd,j}} \qquad (3)$$

After the calculation, we get ∂ =1.05 at T_{sub}=600 ℃; T_{sou}=640 ℃;

The growth rate(um/min) can be calculate from the material flux by

$$G(um/\min) = \alpha J_{cd}\frac{M_{CdTe}}{\rho_{CdTe}}60*10^6$$

Where the coefficient α is sticking coefficient. The fitting parameter value α =0.36[6], M_{CdTe} is molar mass in Kg/mol and ρ_{CdTe} is the density in Kg/m^3.

At the T_{sub}=600 ℃; T_{sou}=640 ℃; h=2mm, 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 Tsou=640 ℃. Table 2 shows the deposition rate and ∂ for different source temperature at Tsub=400 ℃.

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

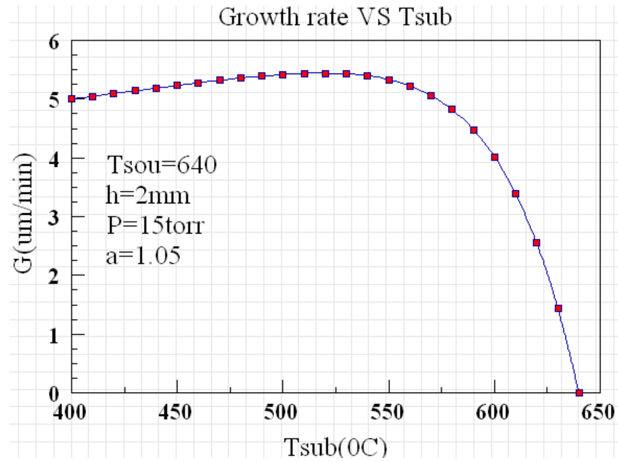

Fig. 4. The growth rate at different substrate temperature

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

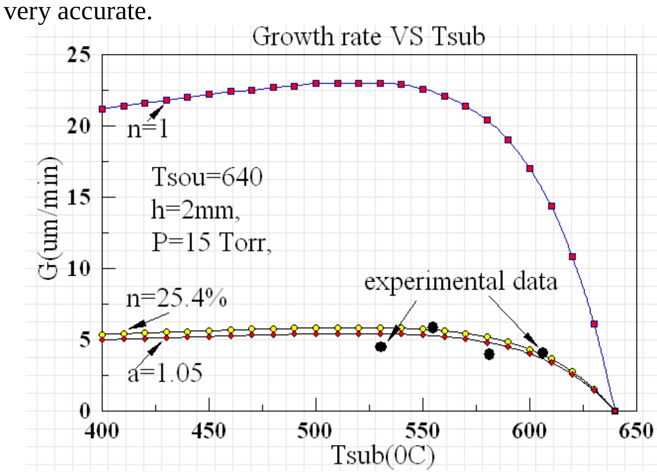

Fig. 5. The growth rate compare with experimental data

TABLE 1
THE DEPOSITION RATE AT DIFFERENT SUBSTRATE TEMPERATURE(Tsou=640 ℃)

T_{sub} (℃)	400	410	420	430	440	450	460	470	480	490	500	510	520
G (um/min)	5	5.05	5.10	5.14	5.19	5.23	5.28	5.32	5.36	5.39	5.42	5.44	5.44

T_{sub} (℃)	530	540	550	560	570	580	590	600	610	620	630	640
G (um/min)	5.43	5.40	5.33	5.22	5.06	4.82	4.48	4.02	3.39	2.55	1.44	0

TABLE 2
THE DEPOSITION RATE AND α AT DIFFERENT SOURCE TEMPERATURE(Tsub=400 ℃)

T_{sou} (℃)	400	410	420	430	440	450	460	470	480	490	500	510	520
δ	2	1.071	1.07	1.069	1.068	1.067	1.065	1.064	1.063	1.062	1.061	1.06	1.059

G(um/min)	0	0.0003	0.0009	0.0018	0.0033	0.0055	0.0089	0.0139	0.0215	0.0325	0.0486	0.072	0.104

T_{sub} (℃)	530	540	550	560	570	580	590	600	610	620	630	640
δ	1.058	1.057	1.056	1.055	1.054	1.053	1.052	1.051	1.05	1.049	1.048	1.047
G(um/min)	0.151	0.216	0.306	0.43	0.6	0.83	1.138	1.551	2.1	2.82	3.768	5

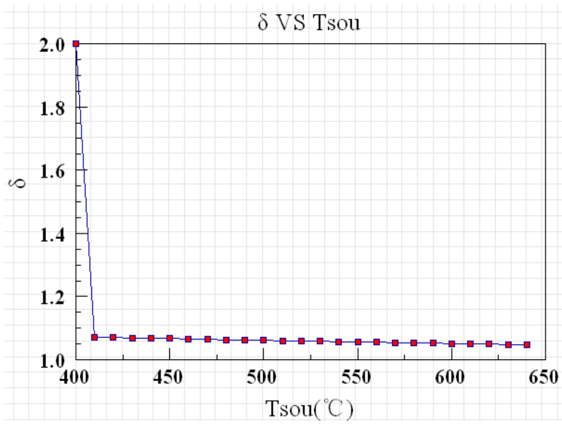

Figure 6 ∂ for different source temperature at Tsub=400 ℃

Figure 6 shows that the ratio ∂ decreases with the increase of the Tsou.

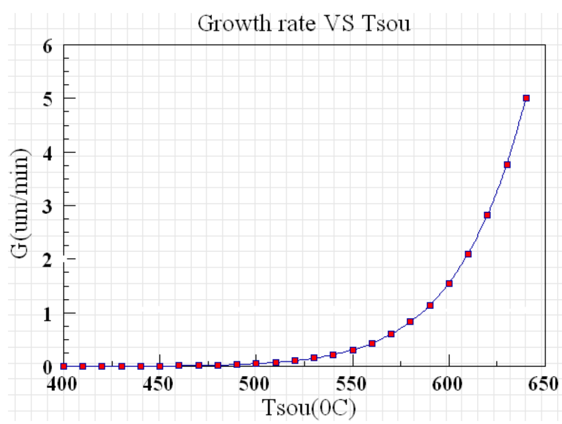

Figure 7 the growth rate VS Tsou at Tsub=400 ℃

Figure 7 shows that the growth rate increases with the increase of Tsou. When Tsou is between 400 ℃-500 ℃, the growth rate is amost zero, because CdTe evaporate very slowly. After 500 ℃. CdTe evaporate faster and the growth rate increase fast.

VI. Conclusion

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

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