# A Model for the Growth of CdTe by Metal Organic Chemical Vapor Deposition

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A kinetic model for the metalorganic chemical vapor deposition (MOCVD) growth of CdTe over a wide temperature range is presented. The model yields the growth rate as a function of the gas-phase concentrations of the constituents. The model is corroborated with experimental results obtained by the MOCVD growth of CdTe at 380° C. The major features of the model are the observed two-step surface-controlled pyrolysis and surface saturation, leading initially to a growth rate that increases with the square root of the concentrations of the reacting species and subsequently to a decrease of the growth rate as the concentrations increase. At even higher concentrations, an additional increase of growth rate is observed and modeled.

**Key words:** MOCVD, CdTe, pyrolysis

This letter presents a kinetic model for the metal-organic chemical vapor deposition (MOCVD) growth of binary compounds such as CdTe, over a wide temperature range, that takes into consideration the pyrolysis process. The binary compounds are denoted by AB.

The present model is an extension of the model for high temperature growth where the pyrolysis process can be neglected.[1,2,3] In the case of CdTe and diethyltellurium (DETe), the pyrolysis becomes limiting below approximately 410° C.[4-7]

To model the growth of CdTe below 410° C, the following assumptions are included:

(a) The reaction is surface controlled. This assumption is based on the experimental results reported in Fig. 1, Ref. 2.

(b) The metalorganic molecules are adsorbed to the surface of the substrate via several surface sites. In the case of relatively simple molecules such as DMCd and DETe, two surface sites are involved[4] (see Fig. 1).

(c) The surface-controlled pyrolysis occurs only after the adsorption of the metalorganic molecules at the surface of the substrate.

(d) The metalorganic molecules and the decomposed Cd and Te compete for the same surface sites. Thus, accumulation of the metalorganic molecules at the surface of the substrate may lead to "surface saturation."

Assumption (a), i.e. surface control, is described by

$$C_{MA}^G = C_{MA}^S \qquad (1)$$

$$C_{MB}^G = C_{MB}^S \qquad (2)$$

where $C_{MA}^G$, $C_{MB}^G$ and $C_{MA}^S$, $C_{MB}^S$ are the concentra-

tions (molecules per unit volume) of the metalorganic sources of A and B in the gas-phase in the bulk of the gas and adjacent to the surface, respectively.

The rate equations of the adsorption process described by assumption (b), are
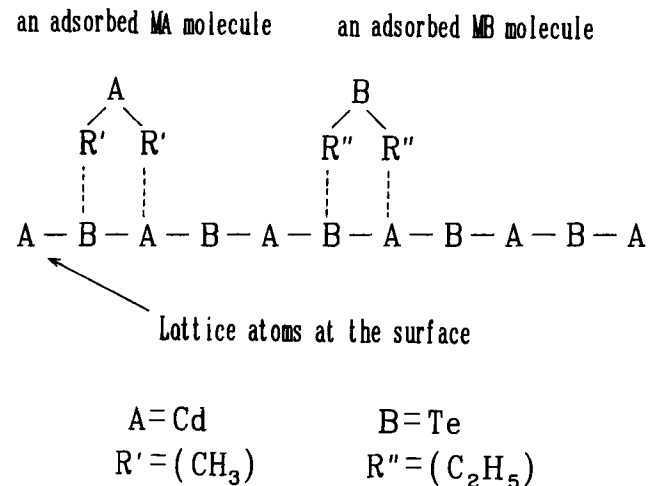
$$\frac{dM_{MA}}{dt} = Q_A C_{MA}^S (M - M_{MA} - M_{MB})^2 - R_A M_{MA}^2 \qquad (3)$$

$$\frac{dM_{MB}}{dt} = Q_B C_{MB}^S (M - M_{MA} - M_{MB})^2 - R_B M_{MB}^2 \qquad (4)$$

where $M_{MA}$ and $M_{MB}$ (molecules per unit area) are the surface concentrations of the adsorbed metalorganic molecules $MA$ and $MB$ (DMCd and DETe in this case), respectively. $M$ is defined as the total number of adsorbed $MA$ and $MB$ molecules that fully cover a monolayer over a unit area of the surface.

The rate Eqs. (3–4) are obtained by two opposing fluxes: The adsorption rate which is proportional to the surface concentration and the number of available empty sites in the power of 2 $\{Q_A C_{MA}^S (M - M_{MA} - M_{MB})^2, Q_B C_{MB}^S (M - M_{MA} - M_{MB})^2\}$ and the desorption rate which is proportional to the number of adsorbed molecules in the power of 2 $\{R_A M_{MA}^2, R_B M_{MB}^2\}$. The origin of the power 2 stems from the assumption that each metalorganic molecule is adsorbed to the surface via two sites.[4] (In the case of more complex metalorganic molecules, higher powers may be required[8]). Each surface atom provides one site that may adsorb either a methyl or ethyl radical (see Fig. 1). Hence, for the case of metalorganic molecules adsorbed on two surface sites, $M = N/2$, where $N$ is the number of lattice atoms per unit area, at the surface. At steady state, $dM_{MA}/dt = 0$ and $dM_{MB}/dt = 0$. Hence, Eqs. (3)–(4) can be solved to yield $M_{MA}$ and $M_{MB}$ expressed using the gas-phase concentrations.

In contrast to the high temperature growth de-

an adsorbed MA molecule      an adsorbed MB molecule

$$A \quad\quad\quad B$$
$$R' \quad R' \quad\quad R'' \quad R''$$
$$A - B - A - B - A - B - A - B - A - B - A$$

Lattice atoms at the surface

$$A = Cd \quad\quad\quad B = Te$$
$$R' = (CH_3) \quad\quad R'' = (C_2H_5)$$

MA : R' − A − R' ;      MB : R'' − B − R'' ;
dimethyl cadmium (DMCd)      dimethyl telluride (DETe)

Fig. 1. — A schematic illustration of metalorganic molecules that are adsorbed at two surface sites. Each surface atom provides one site that may adsorb either a methyl ($CH_3$) or an ethyl ($C_2H_5$) radical. Note: the $B$ atoms of $B \langle 111 \rangle$ CdTe face are displaced by one atomic plane, since for $\langle 111 \rangle$ orientation each monolayer consists of either $A$ atoms or $B$ atoms.

scribed elsewhere,[1,2,3] growth in a lower temperature range is characterized by a complex pyrolysis process that is a limiting factor in the growth process.

The concentrations of the decomposed free atoms $C_A^S$ (Cd) and $C_B^S$ (Te) in the gas-phase at the surface of the substrate, are given by:

$$C_A^S = P_A (M - M_{MA} - M_{MB}) M_{MA} + P_{MA} C_{MA}^S \quad (5)$$

$$C_B^S = P_B (M - M_{MA} - M_{MB}) M_{MB} + P_{MB} C_{MB}^S \quad (6)$$

The terms $P_A (M - M_{MA} - M_{MB}) M_{MA}$ and $P_B (M - M_{MA} - M_{MB}) M_{MB}$ describe the second step of the pyrolysis that occurs on the surface of the crystal. The free sites react and decompose the adsorbed metalorganic molecules. The terms $P_{MA} C_{MA}^S$, $P_{MB} C_{MB}^S$ correspond to the component of the pyrolysis that occurs directly in the gas-phase.[1] The pyrolysis constants $P_{MA}$ and $P_{MB}$ are temperature dependent and are in the range of 0 to 1. The pyrolysis constants $P_A$ and $P_B$ (units of length) depend on temperature as well as crystal orientation and correspond to the pyrolysis that occurs on the surface. The chemical reactions taking place at the surface of the growing film are given by:

$$F_A = K_A C_A^S [(M - M_{MA} - M_{MB})/M] N_B \quad (7)$$

$$F_B = K_B C_B^S [(M - M_{MA} - M_{MB})/M] N_A \quad (8)$$

where the surface-reaction fluxes $F_A$, $F_B$ are related to the concentrations in the gas-phase adjacent to the surface $C_A^S$, $C_B^S$ (molecules per unit volume) and the available sites for adsorption. As in the high

temperature growth model, the model assumes that $N_A$ sites on atoms of type $A$ may adsorb atoms of type $B$, while $N_B$ sites on the atoms of type $B$ may adsorb atoms of type $A$ (see Fig. 2). However, since a fraction of surface sites is involved in the pyrolysis process, the number of sites that participates in the growth process is modified by the ratio $(M - M_{MA} - M_{MB})/M$. The same ratio modifies $N_A$ and $N_B$ since each surface site may adsorb either a methyl or an ethyl radical.
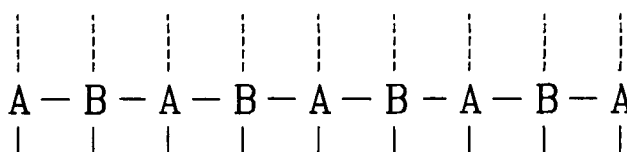
The total number of sites $N$ is constant and is given by

$$N_A + N_B = N \quad (9)$$

surface sites of type $N_A$ and type $N_B$

$$A - B - A - B - A - B - A - B - A$$

(a)
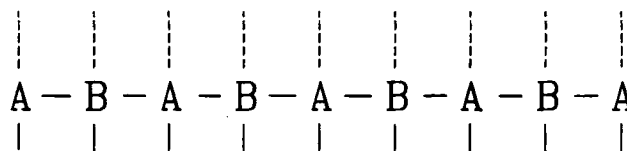
Atoms A and B in the gas-phase adjacent to the surface contributing to $C_A^S$ and $C_B^S$

$$(A) \quad\quad (B)$$

$$A - B - A - B - A - B - A - B - A$$

(b)

Atoms A and B that reacted and are incorporated in the growing layer

$$A \quad\quad\quad\quad B$$
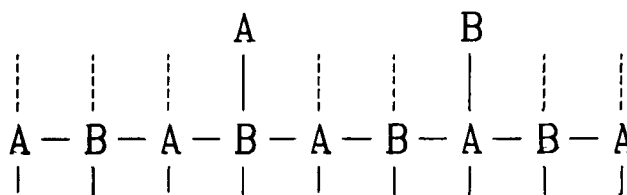$$A - B - A - B - A - B - A - B - A$$

(c)

Fig. 2. — A schematic illustration of: (a) Surface sites for atoms $A$ and $B$ that form the crystal. Each surface atom $A$ provides a surface site of type $N_A$ that adsorbs an atom of type $B$ and each surface atom $B$ provides a surface site of type $N_B$ that adsorbs an atom of type $A$. Note: The $B$ atoms of $B \langle 111 \rangle$ CdTe face are displaced by one atomic plane, since for $\langle 111 \rangle$ orientation each monolayer consists of either $A$ atoms or $B$ atoms. In that case, the $N_A$ sites and the $N_B$ sites are provided by two atomic planes. (b) $C_A^S$ and $C_B^S$ (molecules per unit volume) are the gas-phase concentrations of atoms $A$ and $B$ adjacent to the surface. (c) Atoms $A$ and $B$, adsorbed on atoms $B$ and $A$, respectively, incorporated in the growing layer.

The value of $N$ (sites per unit area) depends on the substrate orientation and is equal to the number of atoms per unit area at a given orientation. For the $B$ face of $\langle 111 \rangle$ CdTe $N = 5 \cdot 10^{14} \text{cm}^{-2}$.

At steady state equal fluxes of $A$ and $B$ are supplied to form layers of the binary compound $AB$. Hence,

$$F_A = F_B \tag{10}$$

The above set of 10 equations enables us to solve the 10 unknowns $F_A$, $F_B$, $C_{MA}^S$, $C_{MB}^S$, $C_A^S$, $C_B^S$, $M_{MA}$, $M_{MB}$, $N_A$, $N_B$, in terms of $C_{MA}^G$, $C_{MB}^G$ and the parameters of the growth and pyrolysis processes $N$, $M$, $Q_A$, $Q_B$, $R_A$, $R_B$, $K_A$, $K_B$, $P_A$, $P_B$, $P_{MA}$, $P_{MB}$.

The growth rate of the epitaxial film is given by

$$V = F_A / m_{AB} \tag{11}$$

where $m_{AB}$ is the number of molecules of the compound $AB$ incorporated into a unit volume of the film.

Under steady state conditions, Eqs. (3–4) yield the surface concentration of the adsorbed metalorganic molecules:

$$M_{MA} = M$$

$$\left[ \frac{\sqrt{Q_A R_B} \sqrt{C_{MA}^G}}{\sqrt{R_A R_B} + \sqrt{Q_A R_B} \sqrt{C_{MA}^G} + \sqrt{Q_B R_A} \sqrt{C_{MB}^G}} \right] \tag{12}$$

$$M_{MB} = M$$

$$\left[ \frac{\sqrt{Q_B R_A} \sqrt{C_{MB}^G}}{\sqrt{R_A R_B} + \sqrt{Q_A R_B} \sqrt{C_{MA}^G} + \sqrt{Q_B R_A} \sqrt{C_{MB}^G}} \right] \tag{13}$$

Equations (7–8) yield that the fluxes of atoms taking part in the chemical reactions at the surface of the growing film, can be expressed by

$$F_A = \alpha N_B \tag{14}$$

$$F_B = \beta N_A \tag{15}$$

where $\alpha$ and $\beta$ are given by

$$\alpha = K_A P_A M^2 (Q_A)^{1/2} R_A R_B^{3/2}$$

$$\left[ \frac{(C_{MA}^G)^{1/2}}{[\sqrt{R_A R_B} + \sqrt{Q_A R_B} \sqrt{C_{MA}^G} + \sqrt{Q_B R_A} \sqrt{C_{MB}^G}]^3} \right]$$

$$+ K_A P_{MA} \sqrt{R_A R_B}$$

$$\left[ \frac{C_{MA}^G}{\sqrt{R_A R_B} + \sqrt{Q_A R_B} \sqrt{C_{MA}^G} + \sqrt{Q_B R_A} \sqrt{C_{MB}^G}} \right] \tag{16}$$

$$\beta = K_B P_B M^2 (Q_B)^{1/2} R_B R_A^{3/2}$$

$$\left[ \frac{(C_{MB}^G)^{1/2}}{[\sqrt{R_A R_B} + \sqrt{Q_A R_B} \sqrt{C_{MA}^G} + \sqrt{Q_B R_A} \sqrt{C_{MB}^G}]^3} \right]$$

$$+ K_B P_{MB} \sqrt{R_A R_B}$$

$$\left[ \frac{C_{MB}^G}{\sqrt{R_A R_B} + \sqrt{Q_A R_B} \sqrt{C_{MA}^G} + \sqrt{Q_B R_A} \sqrt{C_{MB}^G}} \right] \tag{17}$$

It is readily seen from Eqs. (9), (10) and (14)–(15) that

$$N_A = \left( \frac{\alpha}{\alpha + \beta} \right) N \tag{18}$$

$$N_B = \left( \frac{\beta}{\alpha + \beta} \right) N \tag{19}$$

The growth rate is given by

$$V = \left( \frac{\alpha \beta}{\alpha + \beta} \right) \left( \frac{N}{m_{AB}} \right) \tag{20}$$

The growth rate is expressed using gas-phase concentrations of the metalorganic sources $C_{MA}^G$, $C_{MB}^G$ and the growth parameters.

To obtain a physical insight into the factors controlling the growth rate according to the current model, several limiting cases are considered. Assuming that the concentrations of the metalorganic sources are equal and that the growth parameters are the same, (i.e. $\alpha = \beta$) the growth rate is given by

$$V = \frac{\alpha}{2} \frac{N}{m_{AB}} \tag{21}$$

and is shown schematically in Fig. 3. Three regions are observed: At very low concentrations the growth rate is proportional to $(C_{MA}^G)^{1/2}$, $(C_{MB}^G)^{1/2}$, since Eq. (16) can be approximated by

$$\alpha \cong K_A P_A M^2 (Q_A)^{1/2} R_A R_B^{3/2} \left[ \frac{(C_{MA}^G)^{1/2}}{(\sqrt{R_A R_B})^3} \right] \tag{22}$$

With increased concentrations, the terms in the denominator increase and the growth rate passes through a maximum and decreases with

$$\alpha \cong K_A P_A M^2 (Q_A)^{1/2} R_A R_B^{3/2}$$

$$\frac{(1/C_{MA}^G)}{(\sqrt{Q_A R_B} + \sqrt{Q_B R_A})^3} \tag{23}$$

At higher concentrations, the pyrolysis that proceeds directly in the gas-phase becomes more significant and

$$\alpha \cong K_A P_{MA} \sqrt{R_A R_B} \left[ \frac{(C_{MA}^G)^{1/2}}{\sqrt{Q_A R_B} + \sqrt{Q_B R_A}} \right] \tag{24}$$

is observed.

Metalorganic sources that undergo pyrolysis asymmetrically, exhibit a large difference in the pyrolysis constants. In this case, since $P_A \gg P_B$, $P_{MA} \gg P_{MB}$, then $\alpha \gg \beta$ (unless $C_{MA}^G \ll C_{MB}^G$) and the growth rate is limited by $V = \beta\, N/m_{AB}$.

The predictions of the model are compared with the experimental results obtained in a series of growth runs of CdTe at the temperature of 380° C, at less than atmospheric pressure, where the pyrolysis of the metalorganic source DETe is limiting. Figure 4 exhibits the measured data points that correspond to the predictions of the model.

Figure 4a exhibits the growth rate as a function of the concentration of the more easily decomposed metalorganic source (with the larger pyrolysis coefficient), while the concentration of the second source is kept constant. Figure 4b exhibits the growth rate as a function of the concentration of the less easily thermally decomposed metalorganic source while the concentration of the component with the large pyrolysis coefficient is kept constant. The asymmetry in the metalorganic sources is clearly exhibited by the two figures and is easily derived from the equation for the growth rate in the last limiting case.

Epitaxial CdTe layers were grown on the $B$ face of $\langle 111 \rangle$ oriented, undoped CdTe substrates supplied by II–VI incorporated. The substrates were mechanically polished with $0.3\mu m$ alpha alumina powder and subsequently chemically etched for 10 sec by 10% $Br_2$ in methanol solution.

The MOCVD system, custom built by Thomas Swan Co., England, has a horizontal quartz reactor. The metalorganic sources, supplied by Alfa Product, USA, are kept at 25° C. Growth runs were performed with a reactor total pressure of 300 Torr, total $H_2$ flow of 0.65 L/min and a graphite suspector temperature of 380° C.

The growth experiments are characterized by three distinctive features as compared to previously reported studies[5-7] and references therein: relatively low reactor pressure (less than atmospheric pressure); relatively low total flow of carrier gas ($H_2$) and relatively high partial pressure of the metalor-
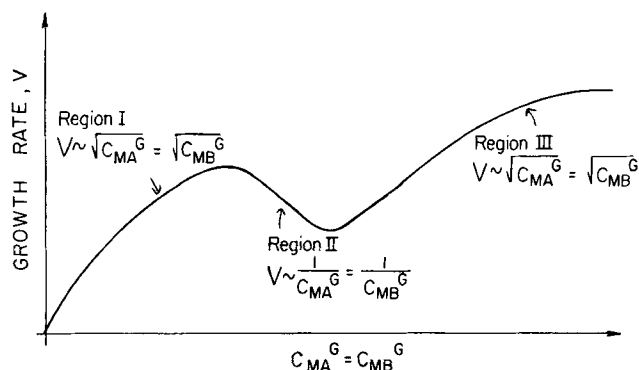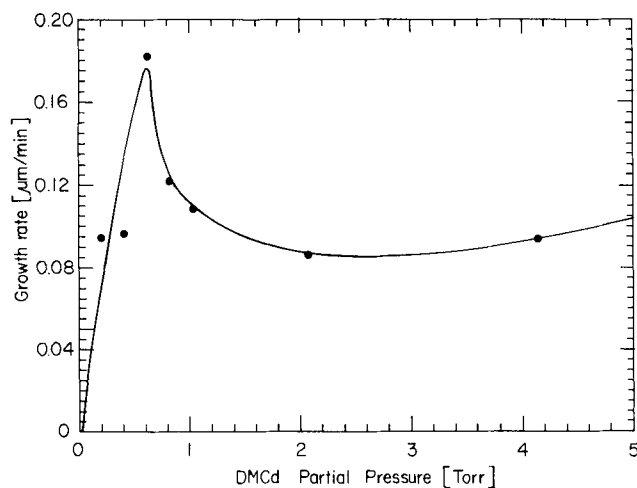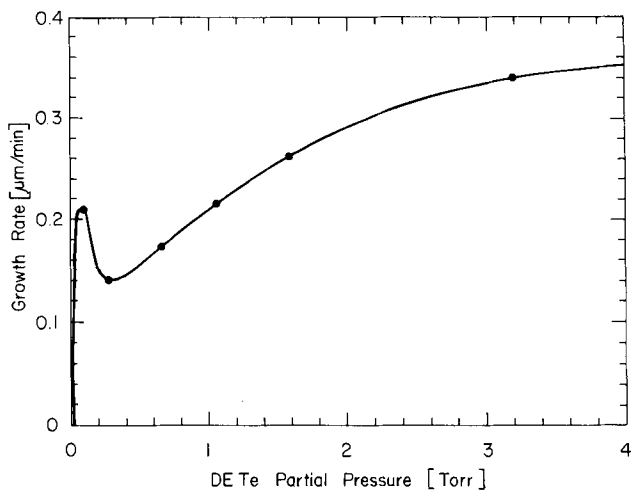
ganic sources (up to 5 Torr). The growth temperature (380° C) is less than the homogeneous pyrolysis temperature of 410° C for DETe.[7]

At these experimental growth conditions, the pyrolysis at the surface of the substrate becomes rate limiting and significant. A similar behavior of the growth rate in the low concentrations region (region I of Fig. 3) was previously observed and reported. Figure 21 of Ref. 4 shows a square-root dependence of CdTe growth rate upon equal and low (less than 1 Torr) gas-phase concentrations ($C_{DMCd}^G = C_{DETe}^G$) at 350° C. To obtain a model for the square root dependence, it was assumed in Ref. 4 that the adsorption of diethyl telluride requires two surface sites. The current study has extended this approach to higher concentrations.



(a)



(b)

Fig. 4. — The dependence of the growth rate epitaxial CdTe on the concentration of the metalorganic source a) The partial pressure of DETe is kept constant at 0.67 Torr. b) The partial pressure of DMCd is kept constant at 0.62 Torr. Growth temperature is 380° C, pressure is 300 Torr. Total flow of carrier gas ($H_2$) is 0.65 I/min. The experimental data is indicated by the points. The solid lines are for visual aid.



Fig. 3. — A schematic description of the growth rate of an epitaxial $AB$ film as a function of the gas-phase concentrations of the sources $C_{MA}^G = C_{MB}^G$ assuming identical growth and pyrolysis parameters for the two sources.

In conclusion, we have presented a simple kinetic model that describes the growth of CdTe by MOCVD, at a reduced temperature range, in which the reaction is surface controlled. The model exhibits the role of the surface sites in the pyrolysis process as well as in the growth process. The competition between these two processes yields a maximum in the growth rate.

At higher temperatures and concentrations, the component of the pyrolysis that occurs directly in the gas-phase (i.e. $P_{MA}C_{MA}^S$, $P_{MB}C_{MB}^S$) becomes more significant. At lower temperatures and concentrations, this component becomes negligible. Hence, the model can be further tailored to fit the high temperature as well as the low temperature growth of CdTe. For the high temperature case two additional equations have to be added to describe the gas-phase mass transport of the metalorganic sources to the crystal surface (assumption (a) is no more valid). In addition, the model can be expanded to describe additional metalorganic sources and binary compounds.

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