A Model for High Temperature Growth of CdTe by Metal Organic Chemical Vapor Deposition

N. AMIR, D. GOREN, D. FEKETE and Y. NEMIROVSKY

Kidron Microelectronics Research Center
Technion-Israel Institute of Technology, Haifa 32000, Israel

A simple kinetic model for the metallorganic chemical vapor deposition (MOCVD) growth of binary epilayers, denoted by AB, is presented. The model yields the growth rate as a function of the gas-phase concentrations of the constituents, in various limiting cases. The model is corroborated with experimental results obtained by the MOCVD growth of CdTe at 480° C. The transition temperature between the surface-reaction and the gas-phase mass-transfer control region is shifted to higher temperature with reduced reactor pressure and increased total flow velocity.

Key words: CdTe, MOCVD, kinetic growth model

This letter presents a simple kinetic model for the metallorganic chemical vapor deposition (MOCVD) growth of binary compounds. The predictions of the model are compared with experimental results obtained by growing CdTe at 480° C.

The model considers the MOCVD growth of binary epilayers, denoted by AB. This notation corresponds to the A (metal) and B (nonmetal) faces often used in the case of $\langle 111 \rangle$ oriented crystals.

The model considers two major processes:[1]

1. Gas-phase mass transfer.
2. Surface adsorption and reaction.

It is assumed that the pyrolysis of the metallorganic sources is not a limiting factor for the temperature range under study.[2] Process (1) is described by the fluxes of the metallorganic sources denoted by MA and MB, from the bulk of the gas phase to the surface of the growing epilayer. The fluxes are approximated by[3,4]

$$f_{MA} = h_{MA}(C^G_{MA} - C^S_{MA}) \qquad (1)$$

$$f_{MB} = h_{MB}(C^G_{MB} - C^S_{MB}) \qquad (2)$$

where C^G_{MA}, C^G_{MB} and C^S_{MB} are the concentrations (molecules per unit volume) of the metallorganic sources of A and B in the bulk of the gas and at the surface, respectively; h_{MA}, h_{MB} are the gas-phase mass-transfer coefficients for the metallorganic sources MA and MB, respectively. These coefficients depend on the reactor design, flow velocity and overall pressure and are only weakly dependent on temperature and the partial pressures of the metallorganic sources.[1]

Process (2) describes the material consumed by the chemical reaction taking place at the surface of the growing film. The surface-reaction fluxes are related to the surface concentrations and the available sites for absorption. The model assumes that N_A sites on atoms of type A may absorb atoms of

type B, while N_B sites on atoms of type B may absorb atoms of type A. The total number of sites N is constant and is given by

$$N_A + N_B = N \qquad (3)$$

The value of N (sites per unit area) depends on the substrate orientation, and can be calculated.

The fluxes of atoms taking part in the chemical reactions at the surface of the growing film, can be approximated by

$$F_A = K_A N_B C^S_A - K'_A N_A C_{AO} \qquad (4)$$

$$F_B = K_B N_A C^S_B - K'_B N_B C_{BO} \qquad (5)$$

where C_{AO} and C_{BO} are the equilibrium concentrations of A and B in the gas phase near the crystal surface, for which no absorption or desorption occurs; C^S_A and C^S_B are the growth concentrations of A and B in the gas phase near the crystal surface. K_A, K'_A and K_B, K'_B are the chemical surface reaction rate constants of absorption and desorption of A and B, respectively, and are strongly dependent upon temperature.

This model describes "high temperature growth" assuming that the pyrolysis of the metallorganic sources at 480° C is complete and hence $C^S_A = C^S_{MA}$, $C^S_B = C^S_{MB}$. There is ample experimental evidence for this assumption; see for example Figs. 1 and 2 in Ref. (2).

It is known[2] that at much reduced temperatures the pyrolysis of DMCd and DETe is mutually assisted, yet since here the pyrolysis is complete we assume independent reaction rates for A and B. We also assumed that the reactions are first order.

In steady state, assuming full decomposition of the metallorganic sources

$$f_{MA} = F_A \qquad (6)$$

$$f_{MB} = F_B \qquad (7)$$

In addition, equal fluxes of A and B are supplied to form layers of the binary compound AB. Hence,

$$F_A = F_B \qquad (8)$$

The above set of eight equations enables us to solve the eight unknowns $f_{MA}, f_{MB}, F_A, F_B, C_A^S, C_B^S, N_A, N_B$.

The growth processes are characterized by the gas-phase mass-transfer coefficients h_{MA}, h_{MB}, the chemical surface-reaction rate constants K_A, K_A', K_B, K_B', the equilibrium concentrations: C_{AO}, C_{BO} and N, the total number of surface sites. The concentrations of the metallorganic sources in the bulk of the gas: C_{MA}^G, C_{MB}^G are determined externally.

The growth rate of the epitaxial film is given by

$$V = F_A / M_{AB} \qquad (9)$$

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

We present a simple case for which $K_A' N_A C_{AO}$ and $K_B' N_B C_{BO}$ can be neglected compared to $K_A N_B C_A^S$ and $K_B N_A C_B^S$. This case corresponds to the high temperature growth of CdTe in our actual experimental setup. Desorption experiments were performed under growth conditions ($T_{sub} = 480°$ C, reactor pressure = 300 Torr and total flow = 500 cc/min in which a CdTe substrate was heated in a H_2 atmosphere. After an hour of heating, no thermal etching or even a slight change in morphology was noticed, using three different samples. In one case, however, a slight thermal etching of 0.2 μm/hr was noticed on one of the samples. We can thus safely neglect the desorption terms in our experiments.

In this simplified case

$$V = \frac{1}{M_{AB}} \cdot C_{MB}^G \cdot \left[\frac{1}{K_B N_A} + \frac{1}{h_{MB}} \right]^{-1} \qquad (10)$$

where N_A is given by[5]

From Eq. (10), the well established two limiting cases[4,8] can be defined:

(1) Mass transfer control for $K_B N_A \gg h_{MB}$, $K_A N_B \gg h_{MA}$. In this case the growth rate depends linearly upon the smaller concentration and is given by

$$V \cong \quad \text{either} \quad \frac{1}{M_{AB}} h_{MA} C_{MA}^G \quad \text{or} \quad \frac{1}{M_{AB}} h_{MB} C_{MB}^G \qquad (14)$$

The concentration of the constituent which determines the growth rate, goes to zero at the surface.

(2) Surface reaction control for $h_{MB} \gg K_B N_A$, $h_{MA} \gg K_A N_B$. In this case the surface concentrations approach the gas-phase concentrations, and the growth rate is given by

$$V = N K_A K_B C_{MA}^G C_{MB}^G / (K_A C_{MA}^G + K_B C_{MB}^G) \cdot \frac{1}{M_{AB}} \qquad (15)$$

for $K_B C_{MB}^G \gg K_A C_{MA}^G$.

$$V \cong N K_A C_{MA}^G \cdot \frac{1}{M_{AB}} \qquad (16)$$

In the special case where $C_{MB}^G \cong C_{MA}^G$ and both concentrations are changed simultaneously, we obtain:

$$V \cong N \frac{K_A K_B}{K_A + K_B} \cdot C_{MA}^G \cdot \frac{1}{M_{AB}} \qquad (17)$$

In the region where $K_A C_{MA}^G \cong K_B C_{MB}^G$ and one of these concentrations is changed while the other is kept constant, the growth rate is sublinearly dependent upon the varying concentration.

Equations (14), (16) and (17) predict that the film growth rate V is proportional to the gas concentra-

$$N_A = \frac{1 + N \dfrac{K_B}{h_{MA}} \dfrac{C_{MB}^G}{C_{MA}^G} - N \dfrac{K_B}{h_{MB}} + \dfrac{C_{MB}^G}{C_{MA}^G} \dfrac{K_B}{K_A} \pm \sqrt{\left(1 + N \dfrac{K_B}{h_{MB}} - \dfrac{C_{MB}^G}{C_{MA}^G} N \dfrac{K_B}{h_{MA}} - \dfrac{C_{MB}^G}{C_{MA}^G} \dfrac{K_B}{K_A}\right)^2 + 4 \dfrac{C_{MB}^G}{C_{MA}^G} \dfrac{K_B}{K_A}}}{2 \left(\dfrac{K_B}{h_{MA}} \cdot \dfrac{C_{MB}^G}{C_{MA}^G} - \dfrac{K_B}{h_{MB}}\right)} \qquad (11)$$

If concentration values are such that the denominator in Eq. (11) is zero, the mathematics reduces to a first-order equation whose solution is:

$$N_A = N(1 + K_B C_{MB}^G / K_A C_{MA}^G)^{-1} \qquad (12)$$

In addition, the surface concentrations are given by

$$C_A^S = C_{MA}^G (1 + K_A N_B / h_{MA})^{-1}:$$
$$C_B^S = C_{MB}^G (1 + K_B N_A / h_{MB})^{-1} \qquad (13)$$

tion C_{MA}^G and C_{MB}^G. The predictions of the model are compared with the experimental results obtained in a series of growth runs of CdTe at the relatively elevated temperatures, at less than atmospheric pressure.

Epitaxial CdTe layers were grown on 1 cm × 1 cm × 1 mm CdTe substrates having ⟨111⟩ orientation supplied by II-VI incorporated.[10] The substrates were prepared by mechanical polishing with 0.3 μm alpha alumina powder and then were chemically etched for 10 sec in 10% Br methanol solu-

tion. The MOCVD system was custom built by "Thomas Swan."[11] The metallorganic sources were supplied by alpha[12] and were kept at 25° C during growth. All growth runs were performed at a reactor pressure of 300 Torr and, unless stated otherwise, with a susceptor temperature of 480° C. Total flow was 500 cc/min in a horizontal reactor 4 cm in diameter.

Figure 1 exhibits the measured growth rate of CdTe as a function of reciprocal temperature. The metallorganic sources are dimethylcadmium—$(CH_3)_2Cd$ and diethyltellurium—$(C_2H_5)_2Te$. The total pressure at the reactor is 300 Torr. Also shown in Fig. 1 are the results of Mullin et al.,[6] who grew CdTe with the same metallorganic sources but at atmospheric pressure. The two sets of experiments are shown in dashed and solid lines, respectively.

In both cases, the plateau in the growth rate indicates the temperature region where the growth is controlled by the gas-phase mass-transfer. The region at lower temperatures, where the growth rate decreases significantly as temperature is reduced, indicates that the growth rate is limited by surface reaction or by the pyrolysis of the metallorganic sources, or both. According to Refs. (2) and (6), a study of the growth rate of epitaxial CdTe using the same metallorganic sources showed that the growth rate was found to be constant from around 500° C down to the order of 350° C. This shows that the pyrolysis of DMCd and DETe is strongly mutually assisted as can be seen compared with Figs. 1 and 2 of Ref. (2). We therefore suggest that the limiting factor in our experiments at lower temperatures is the shift from mass transfer control to surface reaction control. The limiting case of surface-reaction control is changed into mass-transfer control around 370° C for growth at atmospheric pressure and low flow velocities. The change between the two limiting cases occurs at higher temperatures for growth at lower pressures and high flow velocities, since
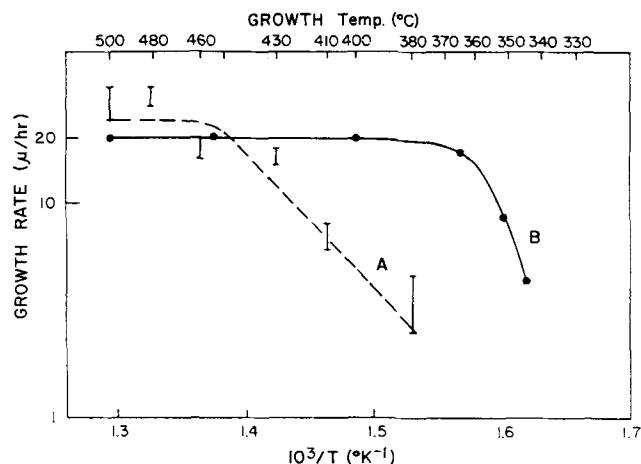
the gas-phase mass-transfer coefficients (h_{MA} and h_{MB}) increase as the pressure is reduced and the flow velocity is increased. For the growth at total pressure of 300 Torr and flow velocity of 20 cm/sec, the change occurs approximately at 450° C. It should be noted that the transition temperature between the two regions depends on additional factors. For example, the reactor design plays a dominant role because the width of the gas boundary layer which determines mass transfer reaction rates is strongly dependent upon flow dynamics.

The dependence of growth rate upon the partial pressures (or concentrations) of the metallorganic sources is also predicted by the model and compared with the experimental results. Figure 2 exhibits the dependence of growth rate upon the concentrations of the sources for a constant ratio of $(CH_3)_2Cd:(C_2H_5)_2Te = 1:(C_{MA}^G = C_{MB}^G)$ at 480° C. Figure 2 exhibits the linear dependence of the growth rate upon concentrations as predicted by the model for growth at elevated temperatures (see Eq. (14)).

Figure 3 exhibits the growth rate at high temperatures for the limiting case of mass-transfer control. The dependence of the growth rate upon the concentration of the metallorganic source with the similar concentration is shown in Fig. 3a for $(CH_3)_2Cd$ and in Fig. 3b for $(C_2H_5)_2Te$. The linear dependence predicted by Eq. (14) is exhibited for both $(CH_3)_2Cd$ and $(C_2H_5)_2Te$ for growth experiments at elevated temperature. Figure 3 indicates that the terms

Fig. 1 — Effect of temperature on growth rate of epitaxial CdTe on CdTe substrates. A. This work B. From the work of Mullin et al.[6]

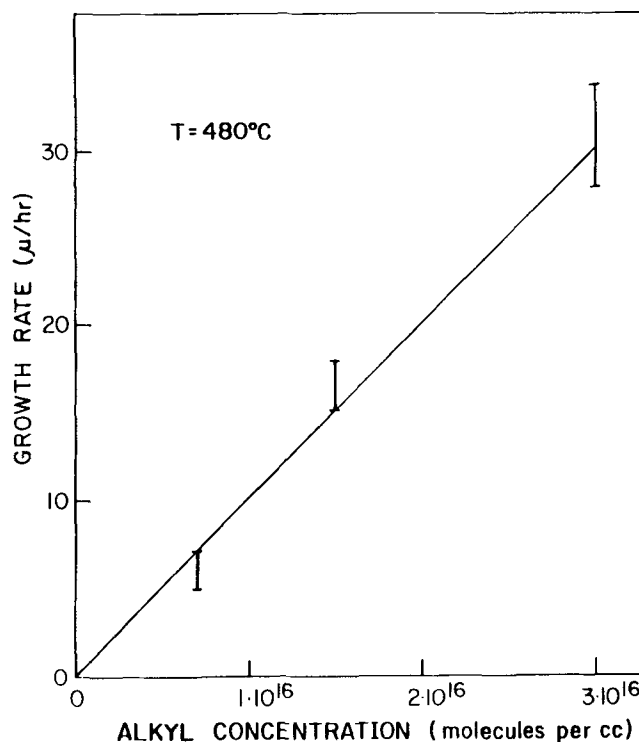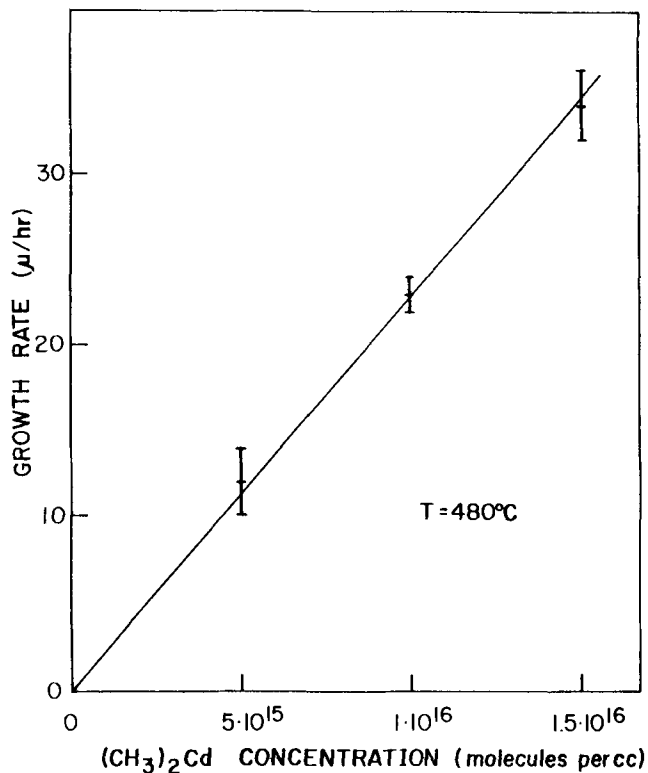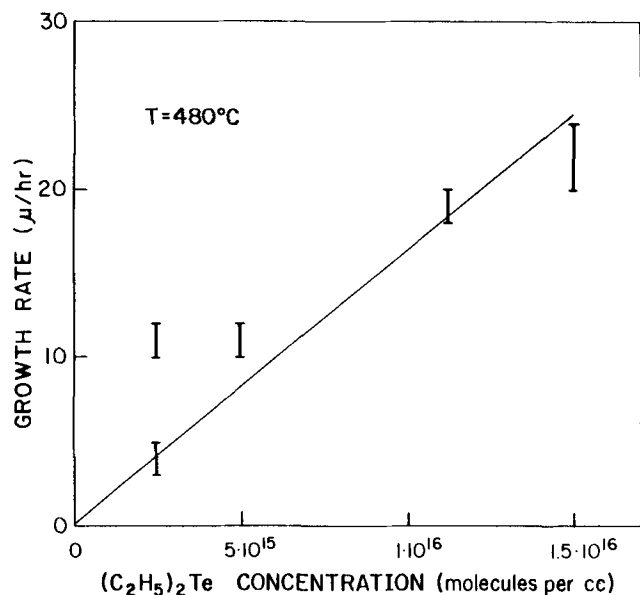Fig. 2 — Dependence of the growth rate of epitaxial CdTe on metallorganic source concentration; the amounts of $(CH_3)_2Cd$ and $(C_2H_5)_2Te$ being equal. Growth temperature is 480° C, pressure is 300 Torr.

(a)

(b)

Fig. 3 — Growth rate of epitaxial CdTe as a function of A. $(CH_3)_2Cd$ concentration while $(C_2H_5)_2Te$ concentration is kept constant at 10^{17} molecules per cc, and B. $(C_2H_5)_2$ Te concentration while $(CH_3)_2$ Cd concentration is kept constant at 10^{17} molecules per cc. Growth temperature is 480° C, pressure is 300 Torr.

$K'_A N_A C_{AO}$ and $K'_B N_B C_{BO}$ of Eqs. (4) and (5) can be neglected, since the growth line goes through the origin of the axes and threshold concentration cannot be detected for either of the sources at the elevated temperature of 480° C.

From the slopes of the lines of Fig. 3, the values of the gas-phase mass-transfer coefficients h_{MA} and h_{MB} can be determined. The exact values depend on flow velocity, total pressure and geometry of the reactor. However, the ratio h_{MA}/h_{MB} is a constant and is equal to D_{MA}/D_{MB}, where D_{MA} and D_{MB} are the gas phase diffusion coefficients of the metallorganic sources MA and MB, respectively.[1]

In the case of dimethylcadmium (DM Cd) and diethyltellurium (DE Te) we obtain

$$h_{DETe}/h_{DMCd} = D_{DETe}/D_{DMCd} \cong 0.6$$

The ratio of the gas-phase diffusion coefficients is estimated to be directly related to the collision cross section [9] of the metallorganic source molecules.[5,7] The ratio of the parameters h_{DMCd} and h_{DETe} is derived from the ratio of the slopes of Figs. 3a and 3b and is given by $h_{DETe}/h_{DMCd} = 0.7 \pm 0.1$, which is in reasonable agreement with the predictions of the model.

ACKNOWLEDGEMENT

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