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A Kinetic Model for the Growth of ZnTe by Metal Organic Chemical Vapour Deposition

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A kinetic model for the metal organic chemical vapour deposition (MOCVD) growth of ZnTe is presented, taking into account the competitive adsorption of organometallic precursors. By assuming that diethylzinc (DEZn) and diethyltellurium (DETe) or di-isopropyltellurium (DIpTe) are adsorbed onto the surface by two sites, the model yields the growth rate as a function of the gas-phase concentrations of the constitutents and is corroborated by experimental results obtained by the MOCVD growth (at 400 °C with DETe or 350 °C with DIpTe), which shows asymmetric behaviour: for a given DETe or DIpTe pressure (10^{-4} atm), the growth rate as a function of DEZn partial pressure passes through a maximum, whereas, at the same constant DEZn pressure, the growth rate increases monotonically when the DETe or DIpTe partial pressure increases

Keywords: MOCVD, ZnTe, pyrolysis, kinetic growth model

1 INTRODUCTION

Amongst the studies on the growth of II–VI semiconductors by metal organic chemical vapour deposition (MOCVD), to our knowledge no kinetic studies have been carried our for ZnTe grown from diethylzinc (DEZn) and diethyltellurium (DETe) or di-isopropyltellurium (DIpTe) as precursors. On the other hand, crystal quality characterization (double-crystal X-ray diffraction,[1] photoluminescence spectroscopy,[2–4] electrical properties[4]) are currently reported. The main interest for ZnTe lies in the fact that it acts as starting material in buffer layers of devices for infrared detection or may in future be used as light-emitting diodes. Thus, a control of the kinetic parameters involved in MOCVD growth is required. As for CdTe grown at low temperature from the pyrolysis of dimethylcadmium (DMCd) and DETe,[4,5] in the case of ZnTe a surface-controlled pyrolysis is assumed at 430 °C and below. Below 430 °C, DETe is not fully decomposed in the gas phase or homogeneously pyrolysed.[6] DIpTe, less stable than DETe, is decomposed at lower temperatures.

We describe the experimental growth procedure in Section 2. The effects of temperature and of precursor partial pressures on the ZnTe growth rate are presented in Sections 3 and 4 respectively. The results are discussed in Section 5.

2 EXPERIMENTAL

Growth experiments were performed in a silica vertical atmospheric-pressure reactor. The inner diameter was 50 mm and the length of the reactor was 40 cm. Substrates were heated using a graphite susceptor, via a coil coupled to the radio-frequency generator. Hydrogen was used as a carrier gas with a total flow rate of 1 slm* (standard litre per minute). The substrate temperature was monitored with a type K thermocouple (Chromel/Alumel), inserted into the center of the graphite susceptor. The heteroepitaxial growth of thin ZnTe films was achieved on GaAs (100) substrates. These substrates were degreased in trichloroethylene and etched in a $5H_2SO_4:1H_2O:1H_2O_2$ solution for 30 s. Bubblers containing organometallic (OM) precursors were maintained in a temperature-controlled bath ($T = +5$ °C) and defined amounts of hydrogen

* Units used in this paper include the following: slm, sccm.

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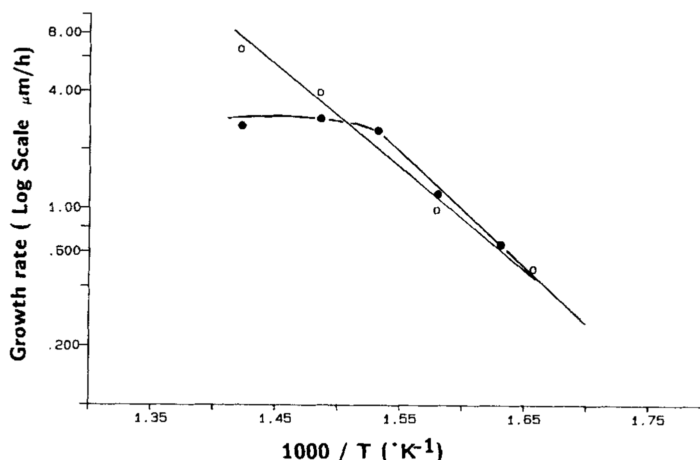

Figure 1 Growth rate as a function of temperature at constant partial pressures $P^{o}_{DEZn} = 1 \times 10^{-4}$ atm for both curves; ○, $P^{o}_{DETe} = 4 \times 10^{-4}$ atm; ●, $P^{o}_{DIpTe} = 4 \times 10^{-4}$ atm.

controlled by mass flowmeters were bubbled through them: the hydrogen flow through the DEZn and DETe or DIpTe flowmeters were respectively in the range 20–40 and 30–150 sccm. The partial pressure of OM species in the reactor was varied from 2.10^{-5} to 5.10^{-4} atm for both precursors. The inlet partial pressure ratio ($\mathcal{R}$ = VI/II) was varied from 0.2 to 5. Before the growth, and after mounting the substrate, the whole system was pumped to 10^{-2} torr to avoid water and oxygen atmospheric contamination. Pure hydrogen gas (less than 4 ppm H_2O) was used as carrier gas. Both precursors were admitted simultaneously in the epitaxial reactor when the desired temperature was reached. The growth temperature ranged from 330 to 430 °C with $\mathcal{R} = 4$. In this temperature range, the growth rate varies exponentially. This thermal behaviour is known[7] to indicate a kinetically limited growth regime with surface reactions. The layer thickness was measured using an optical microscope with a micrometer, and by observing the cleaved cross-section; the typical value was 2–3(±0.2) μm for growths started from DEZn + DETe and 1 – 2(±0.2) μm from DEZn + DIpTe.

3 EFFECT OF TEMPERATURE ON THE GROWTH RATE

Thin layers of ZnTe were grown on GaAs (100) substrates. The DETe and DEZn partial pressures were kept constant at 4×10^{-4} and 1×10^{-4} atm respectively. Figure 1 shows the variation of the growth rate as function of the substrate temperature. The slope of the curve gives an activation energy E_a of about 23 kcal mol^{-1} (96 kJ mol^{-1}) in the low-temperature surface catalytic regime. The activation energy is close to that for the CdTe growth ($E_a = 22$ kcal mol^{-1}) (92 kJ mol^{-1})).[5] At 330 °C, the growth rate is low (0.5 μm h^{-1}) but still measurable, although no homogeneous decomposition of DETe alone occurs. Such behaviour is also found when DETe is replaced by DIpTe, as shown in Fig. 1: $E_a \simeq$ 22 kcal mol^{-1} when keeping OM partial pressure constant at 1×10^{-4} atm ($\mathcal{R} = 1$). This temperature dependence of the growth rate probably corresponds to a two-step mechanism: at low temperatures, the adsorption of molecules is followed by a surface-controlled pyrolysis, whereas gas-phase mass transfer occurs at high temperatures. Our kinetic model of the growth rate will take into account the adsorption of both precursors at low temperature.

It should be noted that the activation energy for the growth is below the binding energy of the first C–metal bond in DEZn and DETe, but of the same order of magnitude as that for breaking the second ethyl–metal bond ($E_2 = 22$ kcal mol^{-1} (92 kJ mol^{-1}) for DEZn, $\simeq 30$ kcal mol^{-1} (126 kJ mol^{-1}) for DETe[8,9]). A few reports on III–V MOCVD growth mechanisms under ultra-high vacuum show that activation energy is also related to energy barrier for the radical desorption from the surface.[10] The poisoning effect of the surface sites by radical adsorption is not taken into account in our model.

4 EFFECT OF PARTIAL PRESSURE ON THE GROWTH RATE

4.1 Basic assumptions

The substrate temperature is fixed at 400 °C when DETe is used and 350 °C with DIpTe. The modelling is based on a few assumptions very close to the model developed by Nemirovski *et al.*[11] for the growth of CdTe at low temperatures:

(1) the reaction is surface-controlled as shown in the preceding section. Hence, Langmuir–Hinshelwood (LH) processes must describe the ZnTe growth more correctly than the Eley–Rideal model which also includes the reaction between adsorbed molecules and precursors in the gas phase;
(2) organometallic molecules are adsorbed to the surface of the substrate via several surface sites. Both for the linear DEZn molecules and the OM species involving tellurium which present an sp^3 hybridization of the Te bonds, two sites are probably required;
(3) the surface-controlled pyrolysis occurs only after the OM molecule adsorption;
(4) the OM molecules and the decomposed products compete for the same surface sites, leading to an accumulation of the organometallic molecules at the surface of the substrate: hence, the desorption is of great importance.

4.2 Relationships between growth rate and partial pressures

Following Germain,[12] assumption (1) is equivalent to:

$$P^{S}_{II} = P^{o}_{II} \qquad [1a]$$

$$P^{S}_{VI} = P^{o}_{VI} \qquad [1b]$$

where P^{S}_{II} and P^{S}_{VI} denote the OM partial pressure in the gas phase near the growing surface, P^{o}_{II} and P^{o}_{VI} the inlet partial pressures.

With a two-site competitive LH mechanism for DEZn, the adsorption rate v^{II}_{a} is given by:

$$v^{II}_{a} = k^{II}_{a} P^{S}_{II}(1-\theta_{II}-\theta_{VI})^2 \qquad [2a]$$

where k^{II}_{a} is the constant of adsorption depending on temperature and sticking coefficient at zero-coverage: θ_{II} and θ_{VI} are classical surface coverages of the corresponding OM.

The desorption rate v^{II}_{d} corresponds to:

$$v^{II}_{d} = k^{II}_{d}\theta^{2}_{II}. \qquad [3a]$$

In the same way, the adsorption and desorption rates of the VI–OM species are calculated, respectively, by:

$$v^{VI}_{a} = k^{VI}_{a} P^{S}_{VI}(1-\theta_{II}-\theta_{VI})^2 \qquad [2b]$$

$$v^{VI}_{d} = k^{VI}_{d}\theta^{2}_{VI} \qquad [3b]$$

Under steady-state conditions, for a species i, we have $v^{i}_{a} = v^{i}_{d}$. Hence, the first equation-set [2]–[3] allows us to express θ_i as functions of both partial pressures:

$$\theta_{II} = \frac{K_{II}\sqrt{P^{0}_{II}}}{1+K_{II}\sqrt{P^{0}_{II}}+K_{VI}\sqrt{P^{0}_{VI}}} \qquad [4a]$$

$$\theta_{VI} = \frac{K_{VI}\sqrt{P^{0}_{VI}}}{1+K_{II}\sqrt{P^{0}_{II}}+K_{VI}\sqrt{P^{0}_{VI}}} \qquad [4b]$$

In these expressions,

$$K_{II} = \sqrt{k^{II}_{a}/k^{II}_{d}}$$

and

$$K_{VI} = \sqrt{k^{VI}_{a}/k^{VI}_{d}}$$

are the ratios of adsorption to the desorption rate constants respectively for II and VI OM species.

From equation (3), we can write the contribution to surface decompositon (dissociative adsorption) and gas-phase pyrolysis in producing atoms near the surface:

$$P_{Zn} = R_{II}(1-\theta_{II}-\theta_{VI})\theta_{II} + X_{II}R^{o}_{II} \qquad [5a]$$

$$P_{Te} = R_{VI}(1-\theta_{VI}-\theta_{VI})\theta_{VI} + X_{VI}R^{o}_{VI} \qquad [5b]$$

This is a two-contribution process. The first term corresponds to adsorbed OM reacting with a free surface site: this reaction is proportional to the product of surface coverage θ_i and to the part of free surface site available. R_i is the reaction constant for surface decomposition. The second term, where X_i represents the percentage of thermal decomposition during co-pyrolysis for i

species, describes the pyrolysis occurring near the surface of the crystal.

In the LH growth model, the two types of adsorbed OM react together in order to give the solid film: it is typically a chemical surface reaction. One may think that one type of atoms (for instance Zn) must find the other surface site type (Te site) to realize a stable bond. We can express the rates of reaction J_{Zn} and J_{Te} for Zn and Te atoms of the surface respectively:

$$J_{Zn} = D_{Zn} P_{Zn}(1 - \theta_{II} - \theta_{VI}) N_{Te} \quad [6a]$$

$$J_{Te} = D_{Te} P_{Te}(1 - \theta_{II} - \theta_{VI}) N_{Zn} \quad [6b]$$

D_{Zn} and D_{Te} are the reaction constants; N_{Zn} and N_{Tn} are respectively the Zn- and Te-atom site numbers per surface area.

In a steady state, equal fluxes of Zn and Te are supplied to form stoichiometric ZnTe layers; we therefore have:

$$J_{Zn} = J_{Te} \quad [7]$$

The growth rate V of the epitaxial film is given by:

$$V = J_{Zn}/m_{ZnTe} \quad [8]$$

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

From Eqns [4]–[6], the rates of reaction are:

$$J_{Zn} = \alpha N_{Te}$$
$$J_{Te} = \beta N_{Zn} \quad [9]$$

where α and β are:

$$\alpha = K_{II} R_{II} D_{Zn} \frac{\sqrt{P^{o}_{II}}}{[1 + K_{II}\sqrt{P^{o}_{II}} + K_{VI}\sqrt{P^{o}_{VI}}]^3} + X_{II} D_{Zn} \frac{P^{o}_{II}}{1 + K_{II}\sqrt{P^{o}_{II}} + K_{VI}\sqrt{P^{o}_{VI}}} \quad [10a]$$

$$\beta = K_{VI} R_{VI} D_{Te} \frac{\sqrt{P^{o}_{VI}}}{[1 + K_{II}\sqrt{P^{o}_{II}} + K_{VI}\sqrt{P^{o}_{VI}}]^3} + X_{VI} D_{Te} \frac{P^{o}_{VI}}{1 + K_{II}\sqrt{P^{o}_{II}} + K_{VI}\sqrt{P^{o}_{VI}}} \quad [10b]$$

In $N = N_{Zn} + N_{Te}$ is the total site number per surface area, depending on the crystallographic orientation, both site numbers can be deduced from Eqns [7] and [9]:

$$N_{Zn} = \left(\frac{\alpha}{\alpha+\beta}\right) N$$
$$N_{Te} = \left(\frac{\beta}{\alpha+\beta}\right) N \quad [11]$$

Finally, the growth rate is expressed as:

$$V = \left(\frac{\alpha\beta}{\alpha+\beta}\right) \frac{N}{m_{ZnTe}} \quad (12)$$

As shown by Eqns [10], α and β contain two terms. The first one is mainly determined by the ratio (K_i) of adsorption to desorption rate constants and the dissociative surface reaction between adsorbed molecules and free sites (R_i). The second one (X_i) contains the pyrolysis contribution. It will be interesting to keep that in mind, when fitting growth rate and experimental values. In contrast with Nemirovski *et al.*,[11] no approximations are made concerning growth parameters (K_i, R_i, D_i, X_i) and partial pressure values.

Setting:

$$A_{Zn} = K_{II} R_{II} D_{Zn} \qquad B_{Zn} = X_{II} D_{Zn} \quad [13]$$

and

$$A_{Te} = K_{VI} R_{VI} D_{Te} \qquad B_{Te} = X_{VI} D_{Te} \quad [14]$$

V is expressed as a function of six parameters: A_{Zn}, B_{Zn}, Z_{II}, A_{Te}, B_{Te}, K_{VI}.

Experimental results were obtained at constant temperature and reactor pressure, so these parameters can be treated as constants. The next step will be to generate, for a given OM partial pressure, growth rate versus the partial pressure of the other OM.

5 Discussion

In the experimental conditions used here, the catalytic reaction at the surface of the growing film is the rate-limiting step of the deposition process, but we also take into account the pyrolytic decomposition of the adsorbed OM species.

Table 1 Parameter values used in the modelling of ZnTe growth

Parameter	DEZn + DETe	DEZn + DIpTe
A_{Zn} (mol s^{-1} $atm^{-1/2}$)	1570 ± 10	990 ± 10
B_{Zn} (mol s^{-1} atm^{-1})	$(5.15 \pm 0.05) \times 10^5$	$(1.2 \pm 0.1) \times 10^6$
K_{Zn} ($atm^{-1/2}$)	700 ± 10	5670 ± 20
A_{Te} (mol s^{-1} $atm^{-1/2}$)	$(5.3 \pm 0.1) \times 10^{-2}$	$(2.9 \pm 0.1) \times 10^{-6}$
B_{Te} (mol s^{-1} atm^{-1})	$(2.32 \pm 0.02 \times 10^5$	$(6.64 \pm 0.05) \times 10^5$
K_{Te} ($atm^{-1/2}$)	20 ± 1	50 ± 2

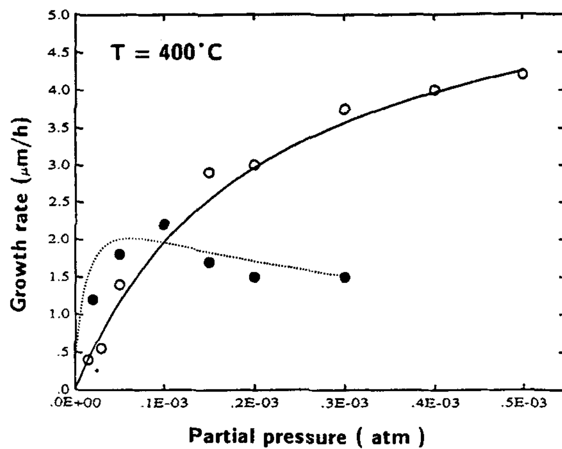

Figure 2 Growth rate as a function of DETe partial pressure ($P^o_{DEZn} = 1 \times 10^{-4}$ atm). Comparison between experiments (○) and model results (solid line). Growth rate is also shown as a function of DEZn partial pressure ($P^o_{DETe} = 1 \times 10^{-4}$ atm (●, experiments; ---, model). The parameters used for the model are reported in Table 1.

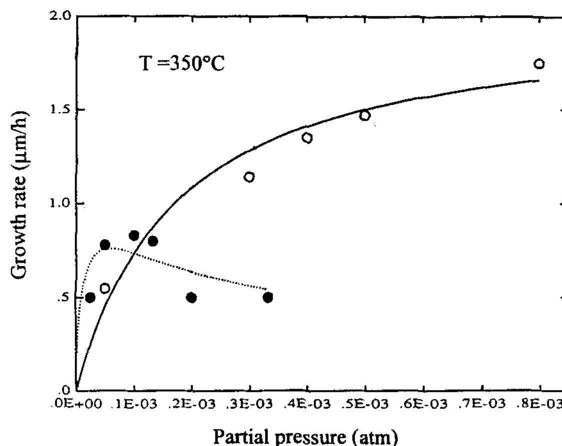

Figure 3 Growth rate as a function of DIpTe partial pressure ($P^o_{DEZn} = 1 \times 10^{-4}$ atm). Comparison between experiments (○) and model results (solid line). Growth rate is also shown as a function of DEZn partial pressure ($P^o_{DIpTe} = 1 \times 10^{-4}$ atm (●, experiments; ---, model). The parameters are also reported in Table 1.

Figure 2 shows a comparison between experimental results and curves calculated with the fitted parameter set reported in Table 1. The DEZn partial pressure and temperature were kept constant at 1×10^{-4} atm and 400 °C respectively. It can be seen that the growth rate varies in a sublinear form when the DETe partial pressure is increased, and does not saturate in the pressure range studied. This behaviour is very close to that described for CdTe.[5] In contrast to Nemirovski *et al.*,[11] no maximum growth rate is observed below $\mathcal{R} = 1$. The analogous comparison, when using DIpTe, is represented in Figure 3 for layers grown at 350 °C.

A more complete computing calculation based on Eqn [12] is also presented in Fig. 4, which represents V versus DETe concentration (broken lines) when the inlet DEZn partial pressure ranges from 5×10^{-5} to 10^{-3} atm. It should be noted that, in the same growth conditions as in our experiments (solid line), V should reach a maximum for $\mathcal{R} \simeq 40$. For greater $\mathcal{R}$-values, the decrease of v can be interpreted as a deficiency in site adsorption for DEZn or its decomposition products. When absolute partial pressure is increased for both precursors, the $\mathcal{R}$ at which maximum growth rate occurs is almost constant.

At constant DETe concentration (1×10^{-4} atm), both experimental and calculated V values, as a function of DEZn concentration, present a maximum at $\mathcal{R} \simeq 1$ (Fig. 2). This growth rate dependence is quite different from the one with constant DEZn concentration. Below $\mathcal{R} = 1$, V decreases and becomes independent of DEZn. With the parameter set of Table 1, the modelling leads to a maximum growth rate at $\mathcal{R} \simeq 1.7$. Difficulties arise for the exact fitting of both DEZn and DETe curves: a better position of the maximum can be obtained, but with less abrupt form, whereas the curve with DEZn constant does not saturate as in our experiments.

The presence of a maximum for V at $\mathcal{R} \simeq 1$ is identical to that observed by Nemirovski *et al.*,[11]

whereas our growth temperature and absolute pressure are different. The independence of V of DEZn ($\mathfrak{R} > 0.5$) is probably due to strong adsorption of this OM. Such hypotheses have been considered by Yasuda *et al.* in the non-competitive adsorption model[13]

The calculated growth rate versus absolute DETe partial pressure (varying from 5×10^{-5} to 1×10^{-3} atm) and DEZn partial pressure is shown in Fig. 5. In this case, the ratio $\mathfrak{R}$ corresponding to the maximum growth rate depends on the absolute DETe concentration. We can see that for $P^{o}_{\mathrm{DETe}} = 5 \times 10^{-5}$ atm, the maximum is reached for $\mathfrak{R} \simeq 1.2$, whereas, for $P^{o}_{\mathrm{DETe}} = 1 \times 10^{-3}$ atm, we note $\mathfrak{R} \simeq 2$. The first set of observations leads to $\mathfrak{R}$ always superior to 1 and a decrease in this ratio when P^{o}_{DETe} increases. This effect correlated to the fitting of Fig. 2 indicates that the higher the absolute partial pressures, the more asymmetric the growth rate between group II and VI OM species. This may be one of the explanations of the experimental curves obtained by Nemirovski *et al.*[11,14]

When DETe is replaced by DIpTe ($P^{o}_{\mathrm{DIpTe}} = 1 \times 10^{-4}$ atm), the maximum of the growth rate V as a function of DEZn partial pressure occurs at $R \simeq 1.7$, as shown in Fig. 3. Then, in our growth conditions, the existence of a V maximum seems to be independent of the Te precursor nature (DETe or DIpTe).

The two parameter sets reported on Table 1 show similar values for Zn parameters except for K_{Zn} ($= 700\ \mathrm{atm}^{-1/2}$ for DETe and $\simeq 5600\ \mathrm{atm}^{-1/2}$ for DIpTe). On the other hand, the A_{Te} parameter corresponding to the adsorption term in Eqn [10b] depends strongly on the nature of the Te–OM species: $A_{(\mathrm{DETe})} = 5.3 \times 10^{-2}\ \mathrm{mol\ s^{-1}\ atm^{-1/2}}$, $A_{(\mathrm{DIpTe})} = 2.9 \times 10^{-6}\ \mathrm{mol\ s^{-1}\ atm^{+1/2}}$. The shapes of the calculated curves are very sensitive to the K parameters.

Because of the high decomposition of all OM species in the reactor ($X_i \simeq 1$), D_{Zn} or D_{Te} may be evaluated from the corresponding B_i parameter value by using Eqn [13] or [14] and R_i is then deduced. Table 2 shows such an evaluation. The atomic surface reaction constants D_i are of the same order in the two systems. In both systems, R_{Zn} is greater than R_{Te}, showing a greater surface reactivity of the DEZn species than the Te ones. Moreover, in the DEZn + DIpTe system, R_i-values are lower than in the DEZn + DETe one; in the former system, the Te reactivity is very weak. The surface coverages (θ_i), calculated with $P_i = 10^{-4}$ atm for all species by putting the K_i values into Eqns [4], are reported in Table 2. The surface appears to be mainly covered by Zn species ($\theta_{\mathrm{Zn}} = 0.85$ and $\theta_{\mathrm{Te}} = 0.02$ in the DEZn + DETe system): a Zn poisoning effect on the surface is then found which could explain the V decreasing for $\mathfrak{R} < 1$. In the DEZn + DIpTe system, this effect is greater. In this latter case, the bigger species size would play the same role: it might be more difficult to attach DIpTe species on the surface than DETe ones.

6 CONCLUSION

Our purpose was to reproduce accurately the experimental determined MOCVD growth rate versus OM concentration at low temperature. We

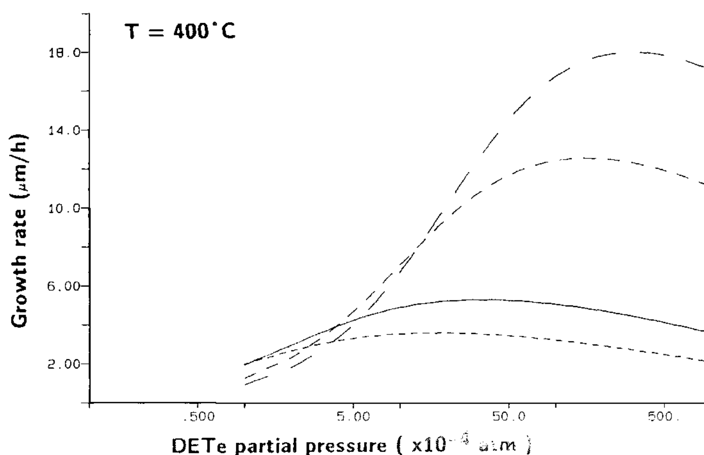

Figure 4 Calculated growth rates as a function of DETe for a given DEZn partial pressure: ----, $P^{o}_{\mathrm{DEZn}} = 5 \times 10^{-5}$ atm; ——, $P^{o}_{\mathrm{DEZn}} = 1 \times 10^{-4}$ atm; ———, $P^{o}_{\mathrm{DEZn}} = 5 \times 10^{-4}$ atm; ————, $P^{o}_{\mathrm{DEZn}} = 1 \times 10^{-3}$ atm.

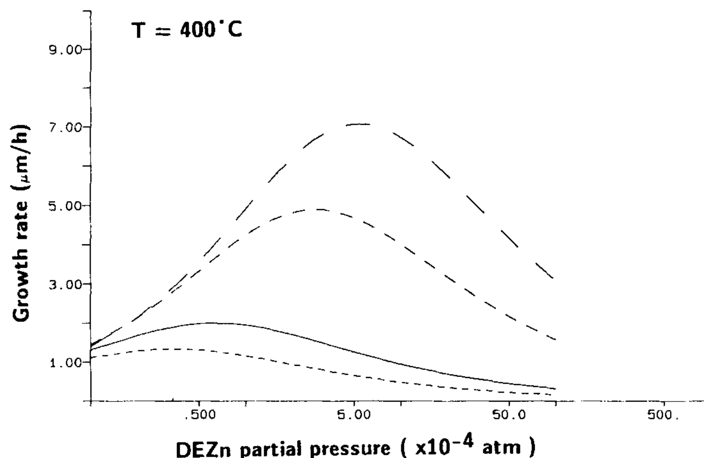

Figure 5 Calculated growth rates as a function of DEZn for a given DETe partial pressure: ----, $P^{o}_{DETe} = 5 \times 10^{-5}$ atm; ——, $P^{o}_{DETe} = 1 \times 10^{-4}$ atm; ———, $P^{o}_{DETe} = 5 \times 10^{-4}$ atm; ————, $P^{o}_{DETe} = 1 \times 10^{-3}$ atm.

have used a Langmuir–Hinshelwood isotherm description. We succeeded in modelling the sublinear variation of the DETe (or DIpTe) concentration at constant DEZn and, less easily, the particular growth rate versus DEZn partial pressure at constant DETe (or DIpTe) input. This different behaviour of growth rate was explained by assuming a two-site competitive adsorption of DEZn and DETe (or DIpTe). Homogeneous decomposition in the gas-phase and surface-catalysed reaction was accounted for in the deposition process. We have also studied the effect of partial pressure range, and we observed a more asymmetric behaviour when the concentration increases. Parameters deduced from this modelling make it possible to calculate surface reaction constants and surface coverages in both systems: a zinc poisoning effect is predicted which can explain the decrease in the growth rate for $\mathfrak{R} < 1$ when DEZn partial pressure is increased. In this initial report, the whole set of surface reactions is not discussed; only experimental data are compared with the fitted data. In the future, knowledge of the surface reaction will probably improve understanding of II–VI MOCVD growth mechanisms.

Table 2 Constant values deduced from the kinetic model of ZnTe growth

Constant	DEZn + DETe	DEZn + DIpTe
D_{Zn} (mol s^{-1} atm^{-1})	5×10^{5}	1×10^{6}
R_{Zn} (atm)	4×10^{-6}	1×10^{-7}
θ_{Zn}[a]	0.85	0.97
D_{Te} (mol s^{-1} atm^{-1})	2×10^{5}	6×10^{5}
R_{Te} (atm)	1×10^{-8}	1×10^{-13}
θ_{Te}[a]	2×10^{-2}	8×10^{-3}

[a] θ values are calculated at 1×10^{-4} atm.

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