

Assessment of a non-linear diffusive–convective model for the ISOVPE MCT growth

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Abstract

Hg_{1–u}Cd_uTe (MCT) is the most important semiconductor for infrared detection. The ISOVPE technique allows good quality MCT epilayers. For technological and scientific reasons it is interesting to have a model which accurately describes this MCT growth technique. Hence, a non-linear diffusion–convection problem which describes ISOVPE MCT film growth was numerically solved by means of discrete mathematics. It has been found that the model describes a diffusion-limited process in accordance with the experimental evidence. As the theoretical and experimental composition profiles were remarkably different in accordance with other authors, it was supposed in the model that a finite rate in the surface reaction enabled a good fit. A numerical value of the surface reaction constant rate was obtained for the experimental conditions of this work which enabled us to determine that the deposition rate has a mixed control. It is expected that the control of the surface reaction rate becomes more important when a lower growth temperature is used. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Hg_{1–u}Cd_uTe (MCT) is an excellent material for the manufacture of infrared detectors. It has a high optical absorption coefficient, a high electron mobility, a low thermal carrier generation rate and a tunable bandgap [1]. Also this material is very suitable for emission devices operating in the 2–5-μm range for which there has been an increasing interest in recent years. In every case the material must be single crystalline. Several bulk and epitaxial growth techniques have been developed to obtain MCT single crystals.

Among the epitaxial techniques — MBE, MOCVD, LPE, ISOVPE — the last one is the most appropriate for small enterprises owing to its low cost and versatility [2]. Besides, this technique produces MCT epitaxial films with good radial compositional uniformity, surface

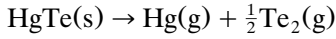
morphology and electrical properties. The interdiffusion process of Cd and Hg in the MCT ISOVPE growth makes necessary a relatively high growth in temperature. An additional inconvenience is that the ISOVPE layers obtained by the standard methods show a composition gradient. Hence, for some device fabrications the deposition stage is followed by high temperature annealings that decrease the composition gradient. As a consequence, it is very useful for the prediction of the compositional profiles. Besides, the prediction and the measurement of the compositional profiles can be used to check certain parameters of the phase diagram and other MCT properties (interdiffusion coefficient, defect distribution, etc.) [1,3]. By these reasons, in this work, we attempted a Djuric model assessment for the prediction of the compositional profiles of ISOVPE MCT films [4].

2. Discussion

2.1. Djuric model

The Djuric model is the most complete and reasonable as a physico-chemical description of the ISOVPE MCT growth technique. The following physicochemical steps are considered [4]:

(1) Source sublimation and dissociation:



Djuric supposed that this step does not determine the film growth rate.

(2) Hg and Te₂ transport from the source to the substrate.

Since the Hg partial pressure is at least three orders of magnitude higher than the Te₂ partial pressure, the rate of this step is controlled by Te₂ transport:

$$v(u, T) = 2 D_{\text{Te}} [P_{\text{Te}}(\text{HgTe}) - P_{\text{Te}}(\text{MCT})] / [kTdN]$$

where D_{Te} is the Te₂ diffusion coefficient in Hg(g) and was calculated using the following equation [4]:

$$D_{\text{Te}} = 2.17 \times 10^{-4} T^{3/2} / [1.66 P_{\text{Hg}}]$$

where

- $P_{\text{Te}}(\text{HgTe})$ and $P_{\text{Te}}(\text{MCT})$ are the Te₂ partial pressures of HgTe and MCT at temperature T ;
- k is the Boltzmann constant;
- d is the source–substrate distance; and
- N is the atomic density of HgTe.

If the Te₂ partial pressures are expressed in terms of the Hg partial pressure and the dissociation equilibrium constants of HgTe and Hg_{1-u}Cd_uTe then:

$$v = 2 D_{\text{Te}} \left[(K_{\text{HgTe}})^2 - (K_{\text{Hg}(1-u)\text{Cd}(u)\text{Te}})^2 \right] / \left[kTdN (P_{\text{Hg}})^2 \right]$$

where

- K_{HgTe} is the HgTe dissociation equilibrium constant; and
- $K_{\text{Hg}(1-u)\text{Cd}(u)\text{Te}}$ is the Hg_{1-u}Cd_uTe dissociation equilibrium constant.

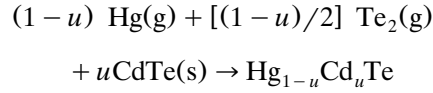
The equilibrium constants were calculated by the following equation [5,6]:

$$K^2(u) = 1.51 \times 10^{33} e^{-40904/T} \times \{(1-u^2)e^{[(4325/T) - 3.598]u^2}\}$$

For the employed experimental conditions ($T = 883$ K; $d = 5 \times 10^{-3}$ m ; no Hg overpressure) the deposition rate results:

$$v = 5.98 \times 10^{-9} [1 - (1-u^2)\exp(1.3u^2)] \text{ m s}^{-1}$$

(3) Reaction at the epitaxial surface:



Djuric supposed that this step does not determine the film growth rate.

(4) Hg and Cd interdiffusion in the epitaxial film with the interdiffusion coefficient

$$D(u) = e^{-(1.53 + 0.51u) \text{ eV}/kT} [7]$$

for the experimental conditions of this work results $D(u) = 1.84 \times 10^{-13} e^{-6.705u} \text{ m}^2 \text{ s}^{-1}$.

In principle, it is reasonable to suppose, as Djuric did, that steps 2 and 4 determine the net rate of the process. Therefore, if the epitaxial surface is chosen as the origin ($x = 0$), a unidimensional diffusion–convection problem results, which is described by the following partial differential equation with non-linear coefficients:

$$\frac{\partial}{\partial x} \left[D(u) \frac{\partial u}{\partial x} \right] - v(u) \frac{\partial u}{\partial x} = \frac{\partial u}{\partial t}$$

2.2. Numerical resolution of the non-linear diffusion–convection problem

The non-linear diffusive–convective partial differential equation has been solved to study the physico-chemical process:

$$\frac{\partial}{\partial x} \left[D(u) \frac{\partial u}{\partial x} \right] - v(u) \frac{\partial u}{\partial x} = \frac{\partial u}{\partial t} \quad (1)$$

- with the initial condition: $u(x, 0) = 1$;
- and the boundary conditions: $D(u) \frac{\partial u}{\partial x} = \square(u) u(0, t)$ at $x = 0$; and
- $u(\infty, t) = 1$,

that mean, Robin boundary condition (or third class condition, in which the unknown value and its gradient appear) and Dirichlet boundary condition (or first class condition, which provides the value of the unknown in a boundary) in a semi-infinite medium.

The equation has been transformed to the form:

$$D(u) \frac{\partial^2 u}{\partial x^2} + \left[D_u(u) \frac{\partial u}{\partial x} - v(u) \right] \frac{\partial u}{\partial x} = \frac{\partial u}{\partial t} \quad (2)$$

where

- $D(u)$ is the diffusive term; and
- $[D_u(u) \frac{\partial u}{\partial x} - v(u)] = V(u)$ is the convective term,

and it has been simultaneously discretized with the boundary conditions. The problem has been solved by the finite differences method employing implicit and explicit procedures [8,9]. In both cases the numerical stability has been analyzed and has shown the consistency of the calculation schemes and the differential problem. The approximate solutions obtained with the two methods are similar.

A very important issue in diffusion–convection problems is that the discretization of the convective term generates numerical dispersion or viscosity. The value of this term adds to the physical diffusion, introducing perhaps an unreal diffusion coefficient [10]. However, the analysis of this value determined that was negligible with regard to the physical diffusion value.

2.3. Comparison between the experimental results and the model predictions: model modification

The growth kinetics of ISOVPE MCT epitaxial films follows a parabolic relation between the layer thickness and the growth time, which is characteristic of a diffusion-limited process [11–17]. In order to analyze if the Djuric model suitably describes the experimental results a study has been made about the behavior of the equation over a wide temperature and pressure range. The diffusion term always controls the equation, resulting in similar behavior to the parabolic heat equation. As a consequence, the Djuric model describes a diffusion-limited process in accordance with the experimental evidence. Fig. 1 shows graphical evidence of the typical behavior for a fixed spacial coordinate with regard to the film surface, of the convective and diffusive terms.

The model was also tested by means of the theoretical and experimental composition profiles comparison. In order to make that comparison, several MCT epitaxial layers were obtained by the ISOVPE technique at 883 K without Hg overpressure over CdTe substrates with different crystalline orientations. The films were clived at {110} preferential crystallographic planes and the composition profiles were determined with a wavelength dispersive electronic microprobe. Additional experimental details and film properties can be found elsewhere [3].

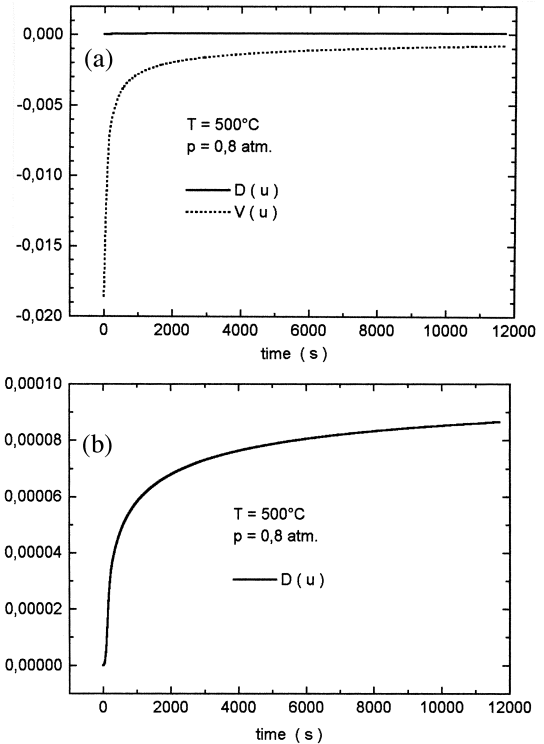


Fig. 1. Diffusive and convective terms in Djuric et al.'s model [4]. (a) Plot of both terms; (b) functional variation of the diffusive term in a small range.

The experimental composition profiles are remarkably different from the theoretical ones. Djuric et al. have argued that the MCT epitaxial films grown in closed ampoules generally have lower thickness because of a surface substrate oxidation [4]. However, other authors have observed a similar discrepancy in MCT epitaxial films grown with hydrogen flow [18]. This experimental result enabled us to neglect that hypothesis. The latter authors have supposed that the surface reaction of step (3) takes place with a slow rate that determines the deposition rate. In this case the deposition rate is the result of two coupled flows: a Te_2 diffusive flow in a Hg vapor phase and a Te_2 chemical reaction flow:

Te_2 diffusive flow:

$$F_1 = D_{\text{Te}_2} (n_{\text{Te}_2}(s) - n_{\text{Te}_2}(u_1)) / d$$

where

- $n_{\text{Te}_2}(s)$ is the Te_2 concentration on the source surface (HgTe); and
- $n_{\text{Te}_2}(u_1)$ is the Te_2 concentration on the MCT layer surface ($\text{Hg}_{1-u}\text{Cd}_u\text{Te}$).

Te_2 chemical reaction flow:

$$F_2 = k_s (n_{\text{Te}_2}(u_1) - n_{\text{Te}_2}^{\text{eq}}(u_1))$$

where

- k_s is the surface reaction rate constant; and
- $n_{\text{Te}_2}^{\text{eq}}(u_1)$ is the Te_2 equilibrium concentration on the MCT layer surface ($\text{Hg}_{1-u}\text{Cd}_u\text{Te}$).

In steady state:

$$F_1 = F_2 = F_3$$

where $F_3 = [1/2] N v'(t)$ is the Te atom flow which is incorporated into the epilayer.

By means of algebra the deposition rate results

$$v'(t) = [2D_{\text{Te}_2}/Nd] \cdot (n_{\text{Te}_2}(s) - n_{\text{Te}_2}(u_1)) \cdot \times \left\{ k_s / [k_s + (D_{\text{Te}_2}/d)] \right\}$$

The ratio between the coefficients k_s and (D_{Te_2}/d) determines the kind of control the deposition rate has:

- if $k_s \gg (D_{\text{Te}_2}/d)$, i.e. mass transfer control, then $v'(t) \sim v(t)$;
- if $k_s \ll (D_{\text{Te}_2}/d)$, i.e. surface reaction control, then $v'(t) \sim v(t) dk_s/D_{\text{Te}_2}$; and
- if $k_s \sim (D_{\text{Te}_2}/d)$, i.e. mixed control, then $v'(t) = v(t) \cdot \{k_s/[k_s + (D_{\text{Te}_2}/d)]\}$.

By means of this considerations the deposition rate results: $v' = jv$, where j is neither a function of u nor of x , hence the results for Eq. (1) are solved in the same way.

Fig. 2 shows the plotted curves corresponding to $j = 1$ (Djuric model with no modification) and that corresponding to $j = 0.6$ which fits the experimental data.

For $j = 0.6$, as $D_{\text{Te}_2}/d = 2.82 \text{ m s}^{-1}$ then $k_s = 4.23 \times 10^{-3} \text{ m s}^{-1}$. Hence, the deposition rate in the experimental conditions had a mixed control. In this sense, it is important that the compositional profiles are similar for MCT epilayers grown over CdTe substrates of

different crystalline orientations. That means that the surface reaction control is important but not decisive. Since chemical reaction rates generally have an exponential temperature dependence while the mass transfer coefficient has a softer dependence, it is expected that the surface reaction control becomes more important when a lower growth temperature is used.

3. Conclusions

The Djuric model describes ISOVPE MCT growth by means of a non-linear partial differential equation with boundary and initial conditions. A numerical analysis of the behavior of such equations over a wide temperature and pressure range enables us to say that the Djuric model suitably describes the experimental result that in the growth kinetics there is a parabolic relation between the layer thickness and the growth time which is characteristic of a diffusion-limited process. The diffusion term always controls the equation, resulting in similar behavior to the parabolic heat equation.

The theoretical and experimental composition profiles have a remarkable difference in accordance with other authors, however, the assumption of a finite rate in the surface reaction determined a good fit in the profiles. A numerical value of the surface reaction rate constant (k_s) was obtained for the experimental conditions of this work which allows us to say that the deposition rate term of the partial differential equation has a mixed control. In this sense it is an important fact that the compositional profiles are very similar for MCT epilayers grown over CdTe substrates of different crystalline orientations. It is expected that the surface reaction control becomes more important when a lower growth temperature is used.

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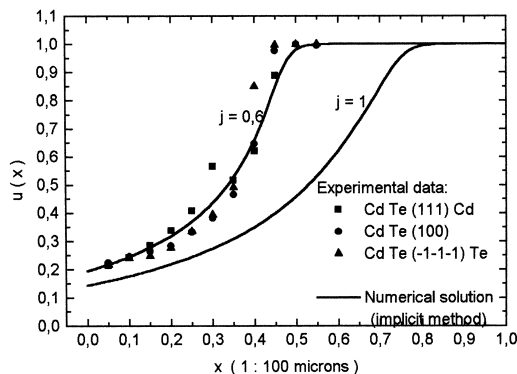


Fig. 2. Theoretical and experimental composition profiles (the modified model with $j = 0.6$ fits the experimental points).

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