

Growth kinetics of ISOVPE HgCdTe epilayers obtained on alloyed CdTe substrates with different crystalline orientations

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ABSTRACT

Hg_{1-x}Cd_xTe (MCT) epilayers were grown on (1 1 1)Cd, (1 1 1)Te, (1 1 0) and (1 0 0) CdZnTe and CdTeSe substrates by isothermal vapor phase epitaxy (ISOVPE). The growth kinetics of the epilayers were studied by a non-linear diffusive convective model for the ISOVPE MCT growth, which was assessed in a previous paper. The non-linear diffusion–convection problem, which describes ISOVPE MCT film growth, was numerically solved by means of discrete mathematics. As the theoretical and experimental composition profiles were remarkably different in accordance with the epilayers grown over pure CdTe substrates, in the model a finite rate in the surface reaction rate constant that enabled a good fit was assumed. The numerical value of the surface reaction rate constant was similar for all the studied substrates and crystalline orientations, hence the results enabled us to determine that the deposition rate has a mixed control for the experimental conditions of this work. This isotropic characteristic of the ISOVPE technique for pure and alloyed CdTe substrates is remarkable, quite different from other MCT growth techniques as MBE or MOCVD.

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1. Introduction

During the last four decades the alloy Hg_{1-x}Cd_xTe (HgCdTe or MCT) has been the most important semiconductor for infrared photodetector production in the 3–30 μm wavelength range. Owing to the technological problems associated with the single crystalline MCT growth, alternative materials such as HgZnTe, HgMnTe, PbSnTe, PbSnSe, InAsSb, and Tl and Bi III–V compounds, have been studied as replacements. However MCT continues being the most important material, and it seems that it will continue to dominate for the production of IR detectors for several reasons: (a) no well-known material has fundamental advantages with respect to MCT since other semiconductor detectors have several orders of magnitude and smaller figures of merit, (b) it is possible to achieve detectors for almost any IR region with an MCT composition change and (c) this fact also allows for dual and multicolour devices [2]. Among the semiconductor alloys of variable energy gap in the IR range, MCT is the one with smaller variation in its lattice parameter. This quasi-independence of the lattice parameter with the composition is one of the main advantages of MCT over other materials [3].

In every case the material must be single crystalline, and ISOVPE technique is the most economical one to grow epitaxial MCT of good quality; therefore, it is the most appropriate method for small companies and laboratories. In spite of the simplicity of the equipment, this technique allows manufacture of considerable variety of IR sensitive devices. Careful work must be done in all stages of the material evaluation, because they are not simple and are interrelated [4]. However, as the ISOVPE layers show a large composition gradient in the perpendicular direction to the epitaxial surface, for some device fabrications, the growth stage is followed by high temperature anneal to decrease it. In a previous paper a model for the ISOVPE MCT growth over pure CdTe substrates was assessed [1]. The aim of this work is to validate the model for the ISOVPE MCT growth on alloyed CdTe substrates.

2. Experimental procedure

Epitaxial MCT was grown by ISOVPE technique over single crystalline (1 1 1)Cd, (1 1 1)Te, (1 1 0) and (1 0 0) CdZnTe and CdTeSe substrates. The growth temperature was (610 ± 1) °C. A growth time of 3.25 h was employed.

The epitaxial films were crystallographically oriented by X-ray diffraction (Laue technique) with a PW3710 Philips diffractometer

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and then perpendicularly cleaved along [110] planes. The compositional profiles were determined with a wavelength dispersive electronic microprobe (CAMECA-SX50) using elemental Cd, Se, Te and Zn as standards. Hg was determined by a relative difference method.

3. Discussion

3.1. Djuric model

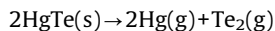
Fig. 1 shows the geometry of the device used for epitaxial growth. It consists of a polycrystalline HgTe source and a single crystalline CdTe, CdZnTe or CdTeSe substrate, separated by distance d . In the space between the source and the substrate, Hg, Cd and Te₂ vapors are present.

The Hg partial pressure is approximately three orders of magnitude higher than the Te₂ pressure and almost five orders higher than the Cd pressure. Here, the Hg pressure is the determinant pressure. Besides, the Cd partial pressure is sufficiently low so that sublimation of this element from the surface of the epitaxial film can be neglected.

Keeping in mind these simple thermodynamic considerations, the model postulates the following steps for the ISOVPE MCT growth [5]:

(a) HgTe sublimation:

If the Hg vapor pressure in the source has values within the region of solid HgTe, the source remains solid but it evaporates dissociatively according to



(b) Te₂ transport in the vapor phase:

Considering that the vapor phase consists of Hg atoms and Te₂ molecules and if it is assumed that the pressure and the temperature remain constant in all the volumes where diffusion takes place, then the Te₂ diffusion coefficient $-D_{\text{Te}_2}^{\text{Hg}}$ – under the experimental conditions and using the rigid sphere model results in SI units:

$$D_{\text{Te}_2}^{\text{Hg}} = \frac{2.17 \times 10^{-4} T^{3/2}}{1.66 P_{\text{Hg}}} \quad (1)$$

(c) formation of Hg_{1-x}Cd_xTe at the surface of the growing epilayer:

Under isothermal conditions the Te₂ molecules are transported by diffusion in a Hg vapor atmosphere. Under such conditions, the Hg vapor pressure remains constant while Te₂ partial pressure decreases from the source toward the substrate.

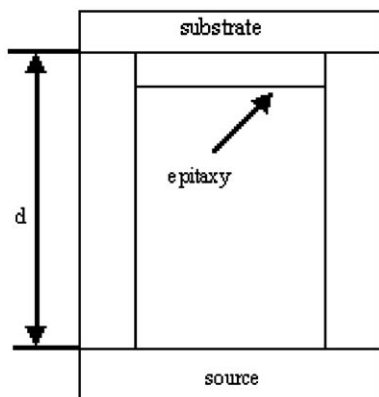


Fig. 1. Geometry of the growth system.

To calculate the epitaxial growth rate, Djuric used the Grove model of thermal oxidation, which postulates three different flows of particles [6]. Fig. 2 presents the different parameters that are involved in the definition of the flows.

Expressing flows in terms of the Te₂ concentration:

$$F_1 = D_{\text{Te}_2} \left(\frac{n_{\text{Te}_2}(x_s) - n_{\text{Te}_2}(x_e)}{d} \right) \quad (2)$$

where F_1 is the Te₂ molecules' flow in the vapor phase and F_2 is the flow of Te₂ molecules consumed by the chemical reaction on the growing epitaxy surface expressed as

$$F_2 = k_s (n_{\text{Te}_2}(x_e) - n_{\text{Te}_2}^{\text{eq}}(x_e)) \quad (3)$$

F_3 is the flow of Te₂ molecules incorporated to the growing epitaxy expressed as

$$F_3 = \frac{1}{2} N v(t) \quad (4)$$

For Eqs. 2–4, d is the source–substrate distance, k_s is the surface reaction rate constant, n_{Te_2} is the corresponding concentration of Te₂ molecules, x_s is the source composition, and x_e is the epitaxy surface composition.

In addition, $n_{\text{Te}_2}^{\text{eq}}(x_e)$ and $n_{\text{Te}_2}(x_e)$ are the Te₂ concentrations in the growing epitaxy in equilibrium and non-equilibrium state, respectively, and N is the number of Te atoms per unit volume. The dimer flow F_3 corresponds, then, to a flow of pairs of atoms, and the factor 1/2 transforms it into a flow of atoms.

In the steady state $F_1 = F_2 = F_3$, therefore by combining Eqs. 2–4 the epitaxial growth rate is

$$v_0(t) = \frac{2D_{\text{Te}_2}}{Ndkt} \left(\frac{P_{\text{Te}_2}(x_s) - P_{\text{Te}_2}^{\text{eq}}(x_e)}{1 + D_{\text{Te}_2}/k_s d} \right) \quad (5)$$

and

$$v_0(t) = v(t) \left(\frac{1}{1 + D_{\text{Te}_2}/k_s d} \right) \quad (6)$$

In Eq. (5) $P_{\text{Te}_2}(x_s)$ and $P_{\text{Te}_2}^{\text{eq}}(x_e)$ are the equilibrium source and epitaxy Te₂ vapor pressures, respectively.

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

- if it is assumed that the reaction rate is not the kinetic controlling step in the global growth process, then $k_s d \gg D_{\text{Te}_2}$ resulting in $v_0(t) \approx v(t)$
- if it is assumed that the reaction rate is the kinetic controlling step in the global growth process, then $k_s d \ll D_{\text{Te}_2}$ resulting in $v_0(t) \approx v(t) d k_s / D_{\text{Te}_2}$
- if it is supposed that the global growth process exhibits a mixed kinetic control, then

$$k_s d \approx D_{\text{Te}_2}$$

resulting in

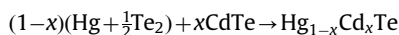
$$v_0(t) = v(t) [k_s / (k_s + D_{\text{Te}_2}/d)] \text{ or } v_0(t) = v(t) j \quad (7)$$

with

$$j = [k_s / (k_s + D_{\text{Te}_2}/d)] \quad (8)$$

(d) interdiffusion between Cd (toward the epitaxy surface) and Hg (toward the substrate bulk):

Over the growing epitaxy surface, Hg atoms, Te₂ molecules and CdTe solid react according to



In order for the reaction to take place, Cd atoms should arrive to the growing layer by interdiffusion between Cd and Hg.

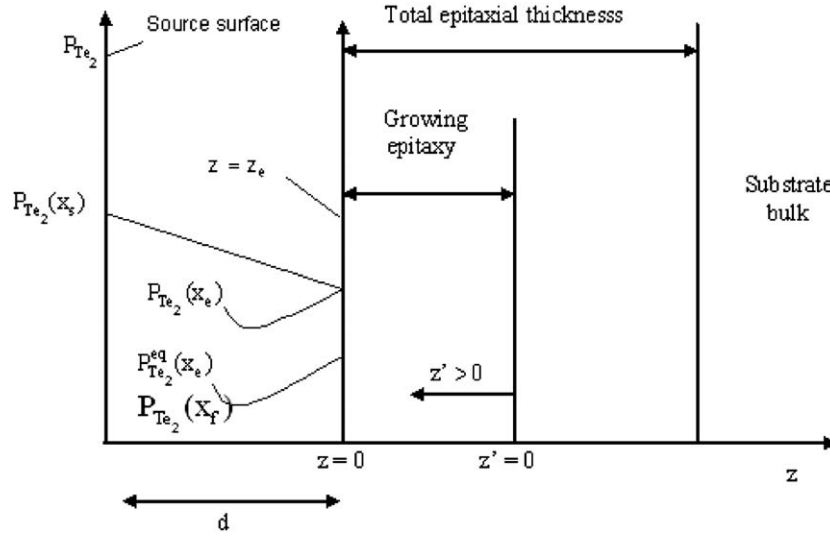


Fig. 2. Schematic representation of ISOVPE process, where $z' = z'_e - z$ and z'_e indicate the epitaxial surface positions.

This process can be described by the Fick second law with an x dependent interdiffusion coefficient.

If a CdTe substrate is used, it has a homogeneous $x=1$ composition for $t=0$. Cd atoms transport in the solid phase is determined by the diffusion equation. Following the notation of Fig. 2, where $z'=0$ indicates the substrate original surface, and $z=0$ is the epitaxy surface:

$$\frac{\partial x}{\partial t} = \frac{\partial}{\partial z'} \left[D(x) \frac{\partial x}{\partial z'} \right] \quad (9)$$

with the initial condition:

$$x(z', 0) = 1 \quad \text{for } z' < 0 \quad (10)$$

and the boundary conditions:

$$\lim_{z' \rightarrow \infty} x(z', t) = 1 \quad \text{and} \quad D(x) \frac{\partial x}{\partial z'} \Big|_{z'=z_e} = - \frac{\partial z'_e}{\partial t} x(z'_e, t) = -v x(z'_e, t), \quad z' \rightarrow \infty$$

The first initial condition indicates that far from the epitaxial film the material is CdTe along the growth process. Meanwhile, the second boundary condition on the growing epitaxy indicates conservation of the Cd total amount in the system along the growth process.

For the mathematical resolution of the problem, it is convenient to make a variable change according to

$$z' = z'_e - z = \int_0^t v dt - z \quad (11)$$

Hence,

$$x(z', t) = x \left(\int_0^t v dt - z, t \right) \quad (12)$$

and,

$$\frac{\partial x}{\partial t} = \frac{\partial}{\partial z'} \left[D(x) \frac{\partial x}{\partial z'} \right]$$

turns into

$$\frac{\partial x}{\partial t} = \frac{\partial}{\partial z} \left(D(x) \frac{\partial x}{\partial z} \right) - v \frac{\partial x}{\partial z} \quad (13)$$

with the initial condition:

$$x(z, 0) = 1 \quad (14)$$

and the boundary conditions:

$$D(x) \frac{\partial x}{\partial z} \Big|_{z=0} = v x(z, t) \Big|_{z=0} \quad (15)$$

and

$$\lim_{z \rightarrow \infty} x(z, t) = 1 \quad (16)$$

The accurate application of the Djuric model to the ISOVPE MCT growth on ternary substrates involves solving systems of differential equations, which increases even more the complexity of the problem. In addition, the necessary experimental information is lacking.

Owing to the low concentrations of Zn (cationic molar fraction = 0.043) and Se (anionic molar fraction = 0.044) in the ternary substrates used in this work [7] and keeping in mind that the epilayer thickness has been shown to be very similar and independent of the substrate used [8], it is reasonable to adopt the following statements:

- the same problem is solved for the films grown over CdTeSe as for the films grown on CdTe, and
- for the epilayers grown on CdZnTe, the problem is similar to that of the epilayers grown on CdTe but with the following modifications:

initial condition

$$x(z, 0) = 0.957 \quad (17)$$

and boundary conditions:

$$D(x) \frac{\partial x}{\partial z} \Big|_{z=0} = v x(z, t) \Big|_{z=0} \quad (18)$$

and

$$\lim_{z \rightarrow \infty} x(z, t) = 0.957 \quad (19)$$

3.2. Numerical resolution of the non-linear problem of diffusion-convection

As presented the problem is a non-linear diffusive-convective partial differential equation with Robin boundary condition and Dirichlet boundary condition in a semi-infinite half-space [9].

The equation was transformed to the following form:

$$D(x) \frac{\partial^2 x}{\partial z^2} + \left[\frac{\partial D(x)}{\partial x} \frac{\partial x}{\partial z} - v(x) \right] \frac{\partial x}{\partial z} = \frac{\partial x}{\partial t} \quad (20)$$

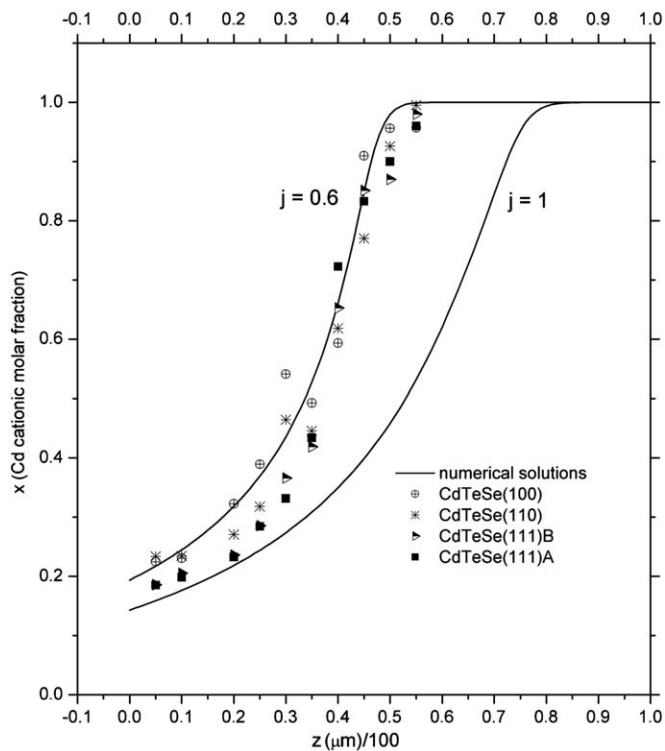


Fig. 3. Experimental and simulated composition profiles with $j=1$ and 0.6 for the MCT epitaxial films grown on CdTeSe (note that symbols are in some cases superimposed on each other).

where $D(x)$ is the diffusive term and

$$\left[\frac{\partial D(x)}{\partial x} \frac{\partial x}{\partial z} - v(x) \right] = V(x) \quad (21)$$

is the convective term.

The values of the equation coefficients, which were calculated according to the experimental conditions, and the methodology used to find the approximate solutions by means of the finite differences method can be found elsewhere [1].

3.3. Comparison between the experimental and simulated composition profiles

A considerable discrepancy between the simulation with the Djuric model without modifications (plotted curves with $j=1$ in Figs. 3 and 4) and the experimental results was found for the epitaxial layers grown over CdZnTe and CdTeSe. These results are in agreement with those reported by us for the layers grown over CdTe, as was described previously [1]. Djuric et al. [10] pointed out the substrate surface oxidation in MCT epitaxial films growth in closed ampoules as the probable cause of smaller films' thickness. However, other researchers have found a similar difference in MCT epitaxial films grown in a hydrogen atmosphere [11]. Hence, it seems reasonable to neglect that hypothesis. A possible explanation of the discrepancy is the deposition rate has a mixed control, as described in Eqs. (7) and (8).

As j is neither a function of x nor of z , the solution for Eq. (20) is obtained in the same way considering the appropriate boundary and initial conditions in each case.

It can be seen in Figs. 3 and 4 that the plotted curves corresponding to $j=0.6$ fit the experimental data. For such j value, $D_{\text{Te}_2}/d = 2.82 \text{ m s}^{-1}$ and $k_s = 4.23 \times 10^{-3} \text{ m s}^{-1}$ are obtained [1]. Hence, it seems reasonable to assume that the deposition rate in our experimental conditions had a mixed control. In this sense,

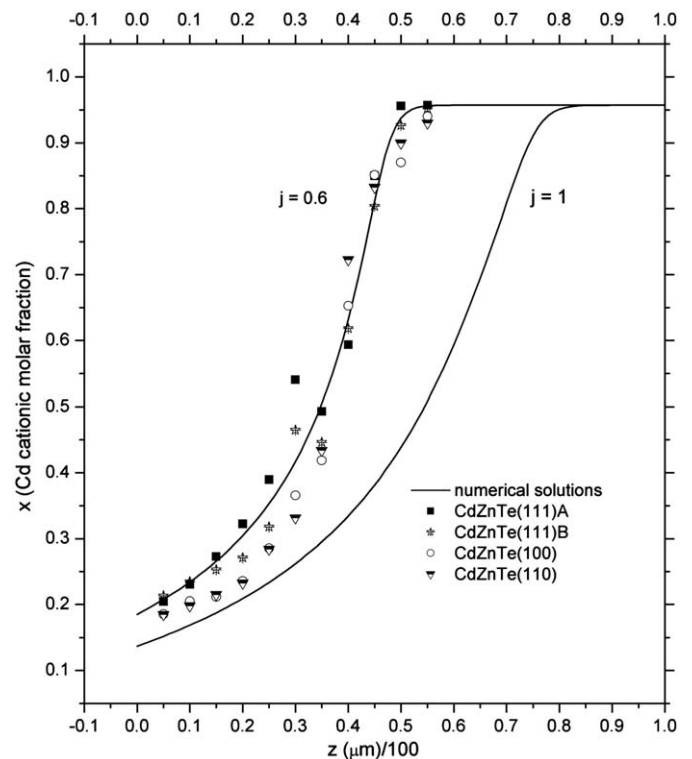


Fig. 4. Experimental and simulated composition profiles with $j=1$ and 0.6 for the MCT epitaxial films grown on CdZnTe (note that symbols are in some cases superimposed on each other).

it is important that the modification in the Djuric model to fit the experimental compositional profiles produces the same results in every case for MCT layers grown on CdTe [1] and alloyed CdTe substrates of different crystalline orientations, indicating that the surface reaction control is important but not decisive. Since chemical reaction rates generally have an exponential temperature dependence, while the mass transport coefficient has a weaker dependence, it is expected that the surface reaction control becomes more important when a lower growth temperature is used.

Very different results have been found in epitaxial MCT obtained by MBE or MOCVD, since the growth kinetics notoriously depend on the substrate crystalline orientation for both pure and alloyed CdTe substrates [12,13]. In the case of MOCVD, the notable differences that can be observed between the growth rates for different crystalline orientations can be explained assuming that surface adsorption and dissociation of the organometallic compounds and the subsequent surface reaction steps are decisive [14]. Meanwhile, for MCT films grown by MBE, the anisotropy of the growth kinetics can be associated with the different surface energy of the diverse crystalline orientations [15].

According to the model used in this work, the growth kinetics isotropy of the ISOVPE technique would be associated with very similar surface reaction rates for the different crystalline planes studied. This determines similar values in the correction factor j and, therefore, also similar values of the surface reaction rate constant k_s for all the crystalline planes studied in this work.

4. Conclusions

A modified Djuric model was used to simulate ISOVPE MCT growth over CdZnTe and CdTeSe substrates. The simulated and experimental composition profiles are significantly different in

accordance with the MCT films grown over CdTe [1]. However, the assumption of a finite rate in the surface reaction led to a good fit in the profiles [1]. The same numerical value, previously obtained for MCT films grown over CdTe, for the surface reaction rate constant (k_s) was found under the experimental conditions of this work for the films grown over all the CdZnTe and CdTeSe substrates with the different crystalline orientations. This fact allows us to say that the deposition rate term of the partial differential equation has a mixed control. Hence, it is expected that for all the substrates the surface reaction control becomes more important when a lower growth temperature is used.

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