

Investigation of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epitaxial vapor phase growth under isothermal conditions

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The $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers were grown by vapor phase epitaxy on Cd-terminated {111} CdTe single crystal substrates from a HgTe solid source under isothermal conditions in a semi-closed system with controlled Hg vapor pressure. The growth kinetics were investigated in the temperature region from 420 °C to 550 °C with different source to substrate spacings, varying from 1 to 11 mm. It was found that the dependence of the growth rate on temperature could be well described by an Arrhenius type equation with an activation energy of 80 kJ/mol in the investigated temperature interval. The activation energies for the crystallization were the same for all the investigated source to substrate spacing. This activation energy value points to the importance of a solid-state diffusion process in the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}/\text{CdTe}$ epitaxial couple obtained by isothermal growth under the given experimental conditions.

Key words: mercury cadmium telluride, isothermal vapor phase epitaxy, two-zone semi closed system, growth rate dependence on temperature.

The narrow-gap semiconductor mercury cadmium telluride ($\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ or MCT) has formed the basis of infrared detection systems for many years starting from its discovery in 1959 by Lawson *et al.*¹ The potential of this material for use in many applications, such as infrared emitters and ultra speed transistors in addition to its well known use in infrared detection, has produced a huge amount of papers dealing with its thin-film growth using variety of epitaxial growth processes, such as MBE (molecular beam epitaxy), MOCVD (metalorganic chemical vapor deposition), LPE (liquid phase epitaxy), ISOVPE (isothermal vapor phase epitaxy), to mention just a few of them.

Among of these processes ISOVPE has shown itself to be a technique with a number of good features. It is a simple and relatively low cost technique for the growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers on large areas CdTe single crystal substrates, furnishing epilayers with excellent surface morphology, high radial composition uniformity and outstanding electronic characteristics.

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The main disadvantage of ISOVPE $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ growth on CdTe substrates is that it produces layers with a composition gradient in the growth direction. The existence of this composition gradient is an inherent growth feature for this epitaxial couple. All efforts are directed towards the experimental control of the composition gradient and surface composition of the epitaxial layers.

In spite of the recent progress in understanding the mechanism of this process^{2,3} which, for the first time, enable the prediction of the composition profiles of the epitaxial layers in dependence on growth parameters, ISOVPE of MCT still poses many questions that have not yet been addressed. It has been shown⁴ that the tellurium diffusion model² should be used with caution. A better agreement between theoretical and experimentally obtained composition profiles of MCT epitaxial layers has been obtained by taking into account both Te_2 diffusion and surface reaction limitations.⁴

The main goal of this work was to supply more experimental results, especially about the temperature dependence of the growth rate, that could lead to a better understand of the mechanism of ISOVPE growth of MCT on CdTe single crystal substrates from a solid HgTe source.

As far as we know, there is only one paper⁵ dealing with the temperature dependence of the growth rate of epitaxial MCT in an open system. In our paper, we stress the importance of the influence of some kind of chemical reaction on the process kinetics as a whole.

EXPERIMENTAL

The isothermal vapor phase growth process

The growth of the ISOVPE layer was performed in a two-zone semi-closed system, described in detail in the literature.⁶ The lower temperature zone contained pure Hg, supplying the required partial pressure of mercury in the growth zone. The partial pressure of the mercury in the growth zone is equal to mercury vapor pressure above the solid Te-rich HgTe and is calculated according to:⁷

$$\log p_{\text{Hg}}(\text{bar}) = 8.280 - 7181/T \quad (1)$$

The geometry of the growth system in the deposition zone is schematically shown in Fig. 1.

The substrates were circular, Cd {111} oriented CdTe single crystal wafers of 1 cm diameter. Immediately before the growth the substrates were treated by a conventional pre-epitaxial procedure including chemical etching in a Br_2 -methanol solution, and rinsing in methanol and deionized water. The growth was performed at temperatures from 420 to 550 °C and the substrate to source spacing was varied between 1 and 11 mm. The growth time was always 2 h.

The as-grown $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers had mirror-like surfaces with a submicron growth relief common for VPE.⁸ The relief was more pronounced when lower growth temperatures were employed.

The thickness of the layers was measured at a {110} cleavage plane under a metallurgical microscope. The interface layer/substrate was well marked without any chemical staining. The growth rate was determined as the ratio between the layer thickness and the growth time.

The sequence of steps generally assumed to occur during isothermal vapor phase epitaxial growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ on CdTe substrates from a HgTe Te-rich solid source is as follows:

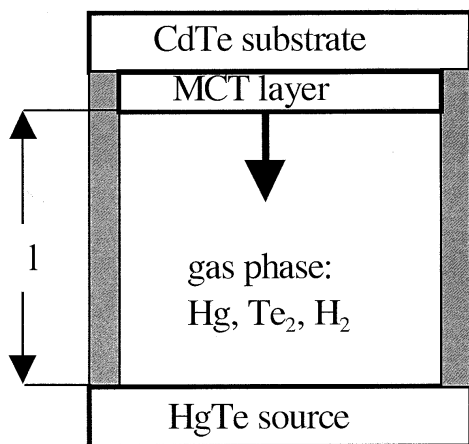


Fig. 1. Deposition zone geometry of the ISOVPE growth system for Hg_{1-x}Cd_xTe.

1. Dissociative evaporation of the HgTe source at the growth temperature:



2. Transport of Te₂ molecules to the substrate (CdTe surface) through the gas phase which consists of Hg atoms and H₂ molecules. The driving force for the transfer of the reactant (Te₂) is the difference in the equilibrium partial pressures of tellurium vapors over the HgTe (source) and over either the substrate (at the very beginning) or the growing layer (during the course of deposition). The tellurium partial pressure over the source is higher than its partial pressure over the substrate.⁹ During the growth process, it remains higher over the source (HgTe) than over the growing layer ($x > 0$).

3. The Te₂ vapor is transported in the direction of this pressure gradient from the source to the substrate during the growth. At the substrate, the vapor in which the mercury partial pressure (p_{Hg}) is constant and equal to the equilibrium mercury pressure over the Te-rich solid HgTe ($p_{\text{Hg,HgTe(s)}}$) is supersaturated in Te₂ vapor and HgTe forms. It is clear that this HgTe formation is a complex process in itself. It includes chemical reaction that involves adsorption of reactants, reaction, surface diffusion and site incorporation. In all this steps substrate surface is of prime significance. In principle, this step can be experimentally distinguished from the physical processes of mass transportation by diffusion.

4. At the surface of the growing layer, the formed HgTe is consumed by reaction with CdTe, which results in formation of a Hg_{1-x}Cd_xTe solid solution. The composition x of this surface layer is determined by the balance between the deposition rate of HgTe and the CdTe supply from the substrate by solid-state interdiffusion. The process of solid state interdiffusion in this couple is strongly compositional dependent.^{10,11}

$$D \text{ (cm}^2 \text{ s}^{-1}\text{)} = 300 \exp(-7.35x) \exp\left(\frac{-185.3 \text{ (kJ/mol)}}{RT}\right) \quad (3)$$

where D is interdiffusion coefficient, R is gas constant, T is the absolute temperature and x is CdTe mole fraction in epitaxial layer.

These steps occur consecutively or in series, and if any step is inherently slower than others, it will determine the overall rate of this process.

The kinetically controlled processes are rate limited by any kind of chemical reaction (for example adsorption or desorption are chemical reactions between the surface and gas phase species). All chemical reactions such as these involve an energy barrier, *i.e.*, they are activated processes. The rates of these processes increase exponentially with temperature following the Arrhenius type of dependence described by the following expression:

$$v = v_0 \exp \left[\frac{-E_a}{RT} \right] \quad (4)$$

where v is the growth rate, v_0 is the pre-exponential factor and E_a is the activation energy of the process.

The activation energies for most processes of the type given above are almost always greater than 42 kJ/mol, usually lying between 105 to 419 kJ/mol.¹²

On the other hand, mass transport processes (such as diffusion in a gas phase) are not nearly as sensitive to temperature changes. In this case the diffusion coefficient of Te_2 molecules in gas phase is proportional to $T^{3/2}$:

$$D_{\text{Te}_2} (\text{cm}^2 \text{ s}^{-1}) = 1.276 \times 10^5 T^{3/2} p_{\text{Hg}}^{-1} \quad (5)$$

where p_{Hg} is in bar.

Thus when the growth rate for gas diffusion controlled processes is plotted in a manner as to yield an "apparent activation energy" the obtained values vary from 12 kJ/mol to 33 kJ/mol.¹²

Based on the above, it appears that the region of kinetic control can be distinguished from the region where the process is mass transport controlled by simply studying the temperature sensitivity of the epitaxial growth rate.

RESULTS AND DISCUSSION

Figure 2 shows that the experimental values of the growth rate dependence on the growth temperature for different values of source to substrate spacing obeys the Arrhenius relationship, Eq. (4). From this plot, the values for the activation energies

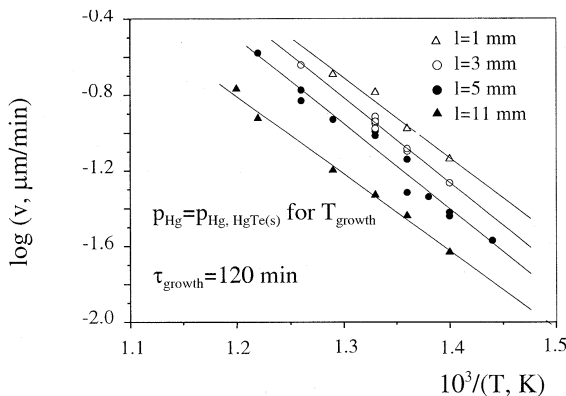


Fig. 2. Temperature dependence of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epitaxial layer growth rate on temperature for different source to substrate spacings.

and pre-exponential factors for each source to substrate spacing (l) can be extracted. After performing such calculations, the following equations describing the growth rate of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layer on the growth temperature are obtained:

$$v \left(\frac{\mu\text{m}}{\text{min}} \right) = 6.24 \times 10^4 \exp \left[-\frac{81.5 (\text{kJ/mol})}{RT} \right] \quad \text{for } l = 1 \text{ mm} \quad (6. a)$$

$$v \left(\frac{\mu\text{m}}{\text{min}} \right) = 6.00 \times 10^4 \exp \left[-\frac{82.7 \text{ (kJ/mol)}}{RT} \right] \quad \text{for } l = 3 \text{ mm} \quad (6. b)$$

$$v \left(\frac{\mu\text{m}}{\text{min}} \right) = 4.66 \times 10^4 \exp \left[-\frac{83.0 \text{ (kJ/mol)}}{RT} \right] \quad \text{for } l = 5 \text{ mm} \quad (6. c)$$

$$v \left(\frac{\mu\text{m}}{\text{min}} \right) = 1.24 \times 10^4 \exp \left[-\frac{78.22 \text{ (kJ/mol)}}{RT} \right] \quad \text{for } l = 11 \text{ mm} \quad (6. d)$$

As can be seen from the experimental results, the activation energy for isothermal vapor phase epitaxial growth of Hg_{1-x}Cd_xTe on CdPTe substrates from a Te-rich HgTe solid source, under the mentioned experimental conditions (the mercury partial pressure in system equal to the mercury vapor pressure above the solid Te-rich HgTe at the growth temperature for a growth time of 120 min) is almost the same (~ 80 kJ/mol) for different substrate to source spacing (from 1 to 11 mm) in the investigated temperature interval (420 °C to 550 °C).

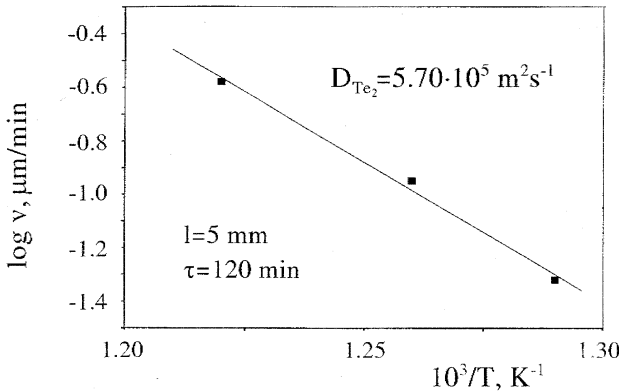


Fig. 3. Temperature dependence of the Hg_{1-x}Cd_xTe epitaxial layer growth rate for experiments in which the mercury partial pressure was adjusted in such way as to yield the same D_{Te_2} for each growth temperature but with the HgTe source still being solid.

Comparing the experimentally obtained values for the activation energy with the literature one (greater than 42 kJ/mol),¹² it can be seen that the reaction of isothermal vapor deposition is in the region of kinetic control under the above mentioned growth conditions. Although there is not enough data to say exactly what the real nature of the rate determining step is, Fig. 3, may be of help in the understanding of this problem.

For the epitaxial growth of MCT when the partial pressure of mercury in the system is equal to the mercury vapor pressure above the solid Te-rich HgTe at the growth temperature, the Te₂ diffusion coefficient, D_{Te_2} , Eq. (5), varies not only because of the change in the growth temperature but also because the mercury partial pressure changes when the epitaxial growth is performed at different temperatures. For example, $D_{\text{Te}_2} = 5.78 \times 10^5 \text{ m}^2 \text{ s}^{-1}$ for a growth temperature of 550 °C and $D_{\text{Te}_2} = 1.72 \times 10^7 \text{ m}^2 \text{ s}^{-1}$ for a growth temperature of 420 °C, when the mercury partial pressure equals the Hg vapor pressure over the solid HgTe at the growth temperature.

We performed several growth runs at different temperatures but with the same D_{Te_2} . For obtaining such growth conditions, we changed Hg partial pressure in system in such a way to obtain desired value of $D_{\text{Te}_2} = 5.70 \times 10^5 \text{ m}^2 \text{ s}^{-1}$ at the different growth temperatures according to Eq. (5). The mercury partial pressure (p_{Hg}) in growth zone was changed by regulating temperature of mercury zone. During changing p_{Hg} in the growth zone, we always must have in mind to choose such a Hg partial pressure as to keep source solid.

Plotting the dependence of the growth rate on temperature for layers grown under the described conditions, as shown in Fig. 3, it can be seen that the activation energy is 205 kJ/mol. The observed value is comparable with the interdiffusion activation energy for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}/\text{CdTe}$ couple of 193 kJ/mol.¹³ Also, our value of activation energy is in good agreement with reported values of activation energy for interdiffusion coefficient, Eq. (3).^{10,11}

It is interesting to compare our results with those from the literature. There are a few results of investigations of the mechanism of this heterogeneous crystallization. In experiments reported in the literature,⁵ the epitaxial layers were grown under similar condition in an open system. Loss of mercury was prevented by using a huge amount of HgTe , which enabled the growth on CdTe substrates under the mercury partial pressure equal to mercury vapor pressure above HgTe at the growth temperature. For isothermal epitaxial growth, which they performed at temperatures from 385 °C to 535 °C, the calculated activation energy was 108 kJ/mol and the pre-exponential factor $1.08 \times 10^5 \text{ } \mu\text{m}/\text{min}$, which are comparable with our results.

Reference⁴ presented a theoretical model of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ISOVPE growth which took into account the Te_2 transport and chemical reaction limitation on the growth rate of the epilayer. According to authors⁴ the rate-limiting step is surface reaction with belonging surface reaction rate constant (k_s). The rate constant of surface reaction for two growth temperatures were estimated in this paper as $k_s = 1.24 \times 10^7 \text{ } \mu\text{m}/\text{h}$ at the growth temperature of 550 °C and $k_s = 1.34 \times 10^7 \text{ } \mu\text{m}/\text{h}$ at the growth temperature of 600 °C. The values of k_s in Ref. 4 were obtained by fitting the experimental data of other authors for composition gradient in epitaxial layer. Presented values for k_s in above-mentioned literature⁴ were the ones that gave the best agreement between their model and the data from the experiments of other authors.

By applying an analytical technique, the rate constants at the two temperatures can be used to create two simultaneous equations in the form: $k_s = k_s^0 \exp [-E_a/(RT)]$, from which the activation energy can be determined as:

$$E_a = \frac{R \ln \frac{k_{s1}}{k_{s2}}}{\frac{1}{T_2} - \frac{1}{T_1}} \quad (7)$$

where the subscripts 1 and 2 denote the appropriate temperatures.

By application of this method to the data from Ref. 4 we obtained $E_a = 9.26$ kJ/mol, which is significantly smaller than our value. A possible explanation is that the source to substrate spacing in Ref.⁴ was 30 mm (approximately threefold larger than ours) and the growth temperature was higher. The discrepancy may simply mean that the same growth mechanism is not operative for large source to substrate spacings and/or at growth temperatures above 550 °C.

CONCLUSION

Layers of Hg_{1-x}Cd_xTe were grown by the isothermal vapor phase epitaxial growth method onto Cd-terminated {111} CdTe single crystal substrates in a semiclosed system from HgTe solid sources. A major problem in the analysis of this heteroepitaxial growth is the large number of variables involved. These include: growth temperature and time, substrate orientation, source composition and its phase state, source to substrate spacing and the mercury partial pressure in the growth zone. To obtain a better understanding of the growth kinetic, we investigated the dependence of the growth rate on temperature for a fixed growth time. During the growth, the mercury partial pressure was fixed and equal to the Hg vapor pressure above the HgTe for the given growth temperature. The growth was performed at temperatures ranging from 420 °C to 550 °C and for different source to substrate spacing, varying from 1 to 11 mm. It was found that the dependence of the growth rate on temperature could be well described by an Arrhenius type equation and with activation energy of 80 kJ/mol in the investigated temperature interval. The obtained activation energy was the same for all the investigated substrate to source spacing. Another set of experiments was performed in which the tellurium diffusion coefficient in gas phase was kept constant for the different growth temperatures. During these experiments, the Hg partial pressure was such that the HgTe source was still solid and the source to substrate spacing was 5 mm. The value of the activation energy obtained from the Arrhenius type dependence of growth rate on temperature, suggested that the growth was limited by solid state diffusion.

ИЗВОД

ИСПИТИВАЊЕ БРЗИНЕ ЕПИТАКСИЈАЛНОГ РАСТА Hg_{1-x}Cd_xTe СЛОЈЕВА ПРИ ИЗОТЕРМСКОМ РАСТУ ИЗ ПАРНЕ ФАЗЕ

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Епитаксијални слојеви Hg_{1-x}Cd_xTe су нарастани из парне фазе на монокристалним подлогама CdTe оријентације Cd{111} из чврстог HgTe извора у изотермским условима у полузатвореном систему са контролисаним напоном паре живе. Кинетика епитаксијалног раста је испитивана у температурном интервалу од 420 °C до 550 °C и при различитим растојањима подлоге и извора која су се мењала у интервалу од 1 до 11 mm. Утврђено је да се зависност брзине раста епитаксијалног слоја од температуре може добро приказати

једначином Аренијусовог типа са активационом енергијом од 80 kJ/mol у испитиваном температурном интервалу. Активациона енергија није зависила од растојања извора од подлоге. Утврђена вредност активационе енергије указује на доминантан утицај дифузије у чврстом стању за $\text{Hg}_{1-x}\text{Cd}_x\text{Te}/\text{CdTe}$ епитаксијални пар који се формира изотермским растом под наведеним условима.

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