Journal of Crystal Growth 62 (1983) 225–229
North-Holland Publishing Company

THERMODYNAMIC ASPECTS OF ORGANOMETALLIC VAPOR PHASE EPITAXY *

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Received 23 September 1982; manuscript received in final form 3 March 1983

Organometallic vapor phase epitaxy (OMVPE) is often thought of as a kinetically-controlled process. In this paper the relationship between the composition of the III/V alloy and the vapor from which it is grown is examined in detail for several systems. For systems of the type $A_xB_{1-x}C$ where A and B are non-volatile group III elements and the V/III ratio in the vapor phase is $\gg 1$ the solid–vapor distribution coefficient is approximately unity and controlled by diffusion of A and B to the growing interface. For mixing on the group V sublattice two cases are observed. When AsH_3 and PH_3 are the group V sources, the rate of pyrolysis of PH_3 determines the distribution coefficient at low growth temperatures. Where the pyrolysis is essentially complete the distribution coefficient is found to be thermodynamically controlled. The relationship between solid and vapor composition can be accurately calculated with no adjustable parameters.

1. Introduction

One of the major advantages of organometallic vapor phase epitaxy (OMVPE) is the ability to easily control solid composition in such systems as $Al_xGa_{1-x}As$. By LPE (liquid phase epitaxy) the Al distribution coefficient is > 100 [1], making the control of solid composition dependent on very tight control of the liquid composition. In OMVPE the Al distribution coefficient is approximately unity [2,3]. An even more dramatic case is $Al_xIn_{1-x}P$ where the very large Al distribution coefficient, calculated to be greater than 10000 [4] would make LPE growth very difficult, if not impossible for reasonably thick layers. In OMVPE we again expect the Al distribution coefficient to be unity [4]. However, the understanding of the physical mechanisms determining the solid–vapor distribution coefficient, k, is not complete. Not all the distribution coefficients in OMVPE systems are unity. In the system $InAs_xP_{1-x}$ the phosphorus distribution coefficient is ~ 0.025 at 600°C [5].

The purpose of this paper is to explore the kinetic and thermodynamic factors which determine the solid–vapor distribution coefficient, k, in OMVPE systems. Perhaps surprisingly, we find that in several cases the dependence of solid composition on vapor composition is accurately calculated using simple thermodynamic models containing no adjustable parameters. This includes the prediction of miscibility gaps in the solid.

2. Growth mechanism

The characteristic of a crystal growth process which best indicates the rate limiting mechanism is the temperature dependence of growth rate. The growth of GaAs using TMGa and AsH_3 is typical of most III/V OMVPE systems. The growth rate is found to be nearly temperature independent over the temperature range commonly used [6,7], indicating that diffusion through the boundary layer to the interface determines the growth rate [4]. This is confirmed by the orientation independence of growth rate [8]. In this regime the ratio of AsH_3 to TMGa in the vapor phase is typically much greater than unity. The growth rate is proportional to the TMGa molar flow rate and independent of the AsH_3 flow rate [4]. Leys and Veenvliet [9] used IR spectroscopy to identify the

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* This work was supported by the Department of Energy, Contract No. DE-AT03-81 ER 10934.

0022-0248/83/0000–0000/$03.00

gas molecules present in the boundary layer. They found only CH_4, indicating that the TMGa is completely decomposed by homogeneous reaction in the vapor phase before reaching the interface. Knowing that the decomposition of AsH_3 occurs very slowly unless catalyzed by the GaAs solid interface [10–12] we suppose the overall reaction to be

$$(CH_3)_3Ga(v) + \tfrac{3}{2}H_2(v) \rightarrow Ga(v) + 3\ CH_4(v), \quad (1)$$

which occurs homogeneously,

$$AsH_3(v) \rightarrow \tfrac{1}{4}\ As_4(v) + \tfrac{3}{2}\ H_2(v), \quad (2)$$

which occurs at the solid–vapor interface, and

$$Ga(v) + \tfrac{1}{4}\ As_4(v) \rightarrow GaAs(s). \quad (3)$$

The input partial pressures are denoted P_i^0 and the near equilibrium partial pressures are denoted P_i. For temperatures above 550°C and $P^0_{AsH_3}/P^0_{TMGa} \gg 1$, the TMGa is thought to decompose totally. The flux of Ga to the surface is then

$$J_{Ga} = D_{Ga}\left(P^0_{Ga} - P_{Ga}\right)/d_b RT, \quad (4)$$

where d_b is the boundary layer thickness and D_{Ga} is the diffusion coefficient for Ga in the vapor phase. Reaction (1) goes to completion at equilibrium, thus $P^0_{Ga} \simeq P^0_{TMGa}$. At the growing interface the mass action expression may be written

$$a^S_{GaAs}/P_{Ga}P^{1/4}_{As_4} = K_{GaAs}. \quad (5)$$

The reaction goes essentially to completion, and since $P^0_{TMGa} \ll P^0_{AsH_3}$, $P_{Ga} \simeq 0$. Thus from eq. (4), $J_{Ga} \propto P^0_{TMGa}$, in agreement with experimental observation. Frolov et al. [13] observed that rotation of the pedestal on which the substrate sits increases the growth rate due to the decrease in d_b.

The growth rate versus temperature behavior for OMVPE growth of GaAs using TMGa plus AsH_3 in the low temperature region is also significant. For $T < 580$°C the growth rate decreases with decreasing temperature and is proportional to the AsH_3, rather than the TMGa, flow rate. Krautle et al. [12] interpret this to be due to the heterogeneous pyrolysis of AsH_3 being the rate limiting kinetic step in the growth process at low substrate temperatures. This will be referred to below.

3. Distribution coefficients

For the growth of $Al_xGa_{1-x}As$ using TMGa and AsH_3, the distribution coefficient, i.e., the ratio of x^s_{AlAs} to x^v_{Al} $(P^0_{TMAl}/P^0_{TMAl} + P^0_{TMGa})$ is found to be approximately unity [2,3]. This can be easily understood in terms of the simple model discussed above. At the interface $P_{Ga} \simeq 0$ and P_{Al} (or $P_{AlAs}) \simeq 0$. The solid composition, x, will be

$$x = \frac{J_{Al}}{J_{Ga} + J_{Al}} \simeq \frac{D_{Al}P^0_{TMAl}}{D_{Ga}P^0_{TMGa} + D_{Al}P^0_{TMAl}}. \quad (6)$$

If $D_{Al} \simeq D_{Ga}$, then $k_{Al} \simeq 1$. This reasoning holds for all alloys where the mixing occurs on the group III sublattice. The partial pressures of Al, Ga and In will all be essentially zero at the growing interface at normal growth temperatures with V/III $\gg$ 1. This is observed experimentally for systems of this type, as illustrated in fig. 1 for the system $Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$ and $Al_xGa_{1-x}Sb$.

For the growth of alloys with mixing on the group V sublattice the situation is somewhat more complex. The rate of pyrolysis of AsH_3 was shown above to be sluggish at low temperatures. The rate of pyrolysis of PH_3 is significantly slower. Mass

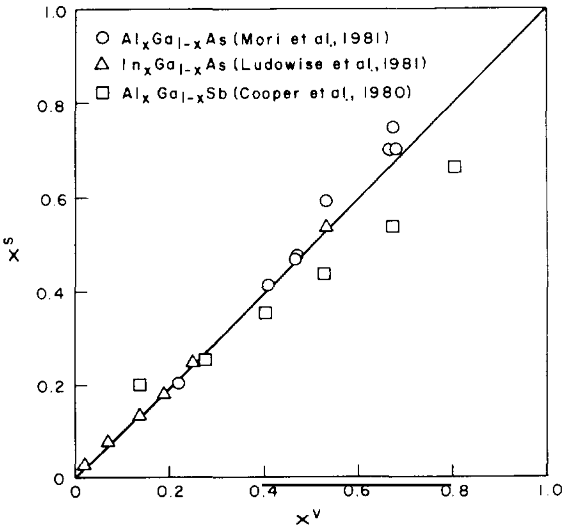

Fig. 1. Solid versus vapor concentration for the III/V alloys: (○) $Al_xGa_{1-x}As$ (data from Mori and Watanabe [3]); (△) $In_xGa_{1-x}As$ (data from Ludowise et al. [14]); (□) $Al_xGa_{1-x}Sb$ (data from Cooper et al. [15]).

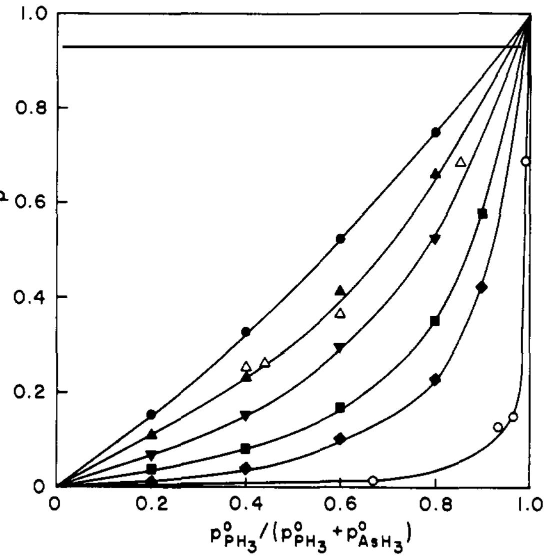

Fig. 2. Solid versus vapor composition for the III/V alloys: (○) $InAs_{1-x}P_x$ at 600°C (Fukui and Horikoshi [5]); (△) $GaAs_{1-x}P_x$ at 750°C (Ludowise and Dietze [17]); and $GaAs_{1-x}P_x$ at 650°C (◆), 700°C (■), 750°C (▼), 800°C (▲) and 850°C (●) (Samuelson et al. [18]).

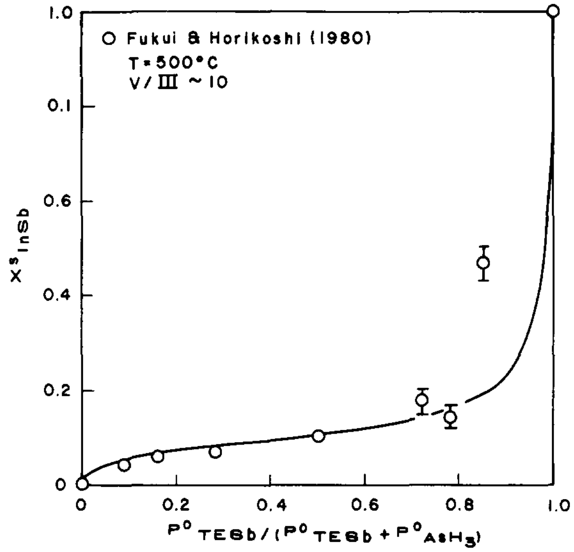

Fig. 3. Solid versus vapor composition for the alloy $InAs_{1-x}Sb_x$. The data are from the work of Fukui and Horikoshi [19]. The solid line was calculated as described in the text using no adjustable parameters.

spectrometric studies [16] show that PH_3 passed through a hot VPE reactor decomposes slowly. At 900°C the decomposition was 85% complete. At 600°C only 25% of the PH_3 was pyrolyzed. As discussed above AsH_3 pyrolysis is much more rapid. In fact, the pyrolysis rate normally controls the phosphorus distribution coefficient in As and P containing alloys grown by OMVPE. This is shown in fig. 2 where $x_P^s$is plotted versus x_P^v for $InAs_{1-x}P_x$ and $GaAs_{1-x}P_x$ at various substrate temperatures. At 600°C a very large ratio of PH_3 to AsH_3 is required to produce alloys with a significant P content. As the substrate temperature increases the P distribution coefficient increases due to the more rapid PH_3 pyrolyis. It becomes approximately equal to unity for a temperature of 850°C in the $GaAs_{1-x}P_x$ system. Thermodynamically, the phosphides are more stable than the arsenides, thus k should be greater than unity.

For III/V alloys where mixing is on the group V sublattice and the pyrolysis is rapid, thermodynamics controls the distribution coefficient. An example is the system $InAs_{1-x}Sb_x$. The data of Fukui and Horikoshi [19] are plotted in fig. 3. The thermodynamic calculation of the Sb distribution coefficient is quite simple. We assume that the pyrolysis of TEIn, TESb and AsH_3 is complete. In addition, we assume equilibrium at the solid/vapor interface, which yields the two mass action expressions

$$a^s_{InSb}/P_{In}P^{1/4}_{Sb_4} = K_{InSb}, \tag{7}$$

$$a^s_{InAs}/P_{In}P^{1/4}_{As_4} = K_{InAs}. \tag{8}$$

Two additional conservation constraints are imposed, one on composition

$$x = \left(P^0_{Sb_4} - P_{Sb_4}\right)\left(P^0_{Sb_4} - P_{Sb_4} + P^0_{As_4} - P_{As_4}\right)^{-1}, \tag{9}$$

and one on stoichiometry

$$P^0_{Ga} - P_{Ga} = 4\left(P^0_{As_4} - P_{As_4}\right) + 4\left(P^0_{Sb_4} - P_{Sb_4}\right). \tag{10}$$

Together we have four equations and four unknowns, x, P_{Ga}, P_{Sb_4} and P_{As_4} for a given temperature and input gas flow rates. The only further consideration is the treatment of the non-ideality of the solid. We simply use the regular solution model where

$$a_i^s = x_i^s \exp\left[(1 - x_i^s)^2 \Omega/RT\right], \tag{11}$$

where Ω is the interaction parameter determined by fitting the liquid–solid phase diagram [1]. In cases where Ω is not available it can be calculated from the DLP model [20].

For the $InAs_ySb_{1-y}$ system, Ω is found to be 2250 cal/mole [1]. The values of K_{InSb} and K_{InAs} were determined from the compilation of Brebrick [21], correcting for the fact that the vapor as opposed to the liquid is in equilibrium with the solid [22]. The values used for 500°C were $K_{InSb} = 244$ and $K_{InAs} = 638$. The solid curve in fig. 3 is calculated with no adjustable parameters. It fits the data extremely well, indicating that the thermodynamic considerations control alloy composition in this system.

A somewhat more complex and interesting system is $GaAs_{1-x}Sb_x$. The experimental data of Cooper et al. [23] are shown in fig. 4. The data show a range of solid composition over which solid alloys cannot be grown at 600°C. Gratton et al. [24] have shown that a miscibility gap exists in this system. The thermodynamic calculation, performed as described above with $K_{GaAs} = 440$ from the data of Panish and Ilegems [1] and Stull and Sinke [22] and $K_{GaSb} = 260$ from the data of Brebrick [21] and Stull and Sinke [22] yields the solid lines shown in fig. 4. The broken line represents the calculated miscibility gap at 600°C. The agreement with the experimental results is quite satisfactory.

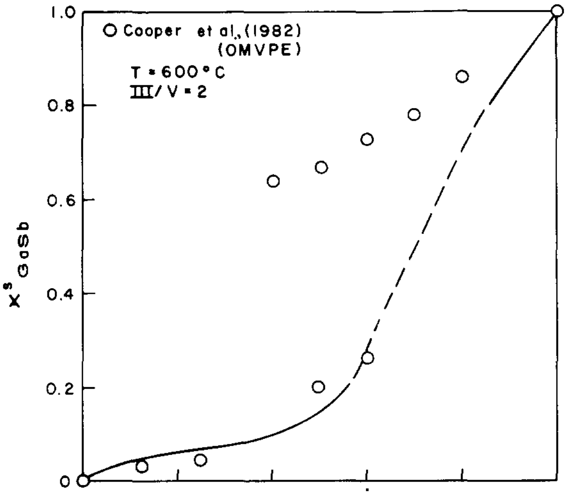

Fig. 4. Solid versus vapor composition for the alloy $GaAs_{1-x}Sb_x$. The data are from the work of Cooper et al. [23]. The solid line represents the calculation described in the text. The broken line represents the extent of the calculated miscibility gap.

It appears that the thermodynamic miscibility gap prevents the growth of certain alloys by OMVPE. The kinetically controlled MBE process apparently allows the growth of alloys throughout the range of immiscibility [25].

A quaternary system which shows the same general behavior is $InP_xAs_ySb_{1-x-y}$, where all mixing is again on the group V sublattice. Data of Fukui and Horikoshi [26] show a large region of solid immiscibility. The thermodynamic calculation of the extent of the miscibility gap (the binodal) has been performed [27] and agrees well with the experimental results.

The existence of these miscibility gaps in III/V alloys has not been thoroughly studied, but apparently represents a significant problem. For the system $Ga_xIn_{1-x}As_yP_{1-y}$, perhaps the most widely used quaternary III/V alloy, the miscibility gap is quite large at ordinary growth temperatures [28]. Preliminary experimental data confirm that in certain ranges of composition, LPE growth is quite difficult [29].

4. Conclusions

The solid–vapor distribution coefficients in III/V alloys grown by OMVPE have been studied systematically. Three general classes of behavior are observed. (1) For alloys of the type $A_xB_{1-x}C$ where A and B are group III elements, when the V/III ratio is large, the composition is determined by the relative diffusion rates of A and B to the growth interface. Since their diffusion coefficients are approximately equal, $k \simeq 1$. (2) For alloys of the type AC_xD_{1-x} where C and D are the group V elements As and P obtained by pyrolysis of AsH_3

and PH_3, the distribution coefficient of P is found to be small, especially at low temperatures. In this case K is determined by the rate of pyrolysis of PH_3. (3) For alloys of the type AC_xD_{1-x} where C and D are group V elements, not involving PH_3, the distribution coefficient is found to be thermodynamically controlled. Simple calculations involving the stability of the solid solution using the regular solution model give good agreement with experimental results with no adjustable parameters. For the system $GaAs_{1-x}Sb_x$, the calculations and experimental data show a miscibility gap. Apparently the range of solid compositions obtainable for the OMVPE growth of III/V alloys is subject to the constraints imposed by the thermodynamic miscibility gap.

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