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Some Phase Boundary Region Correlations in the Liquid Phase Epitaxy Growth Process

In the present work the behavior of n-component liquid phase during the liquid phase epitaxial growth process is considered. As it follows from these considerations, in the liquid phase epitaxy growth one must distinguish two types of components - with a positive concentration gradient and with negative concentration gradient. A possible mechanism for deposition of the components having a negative concentration gradients, for which, in general, the liquid phase is superheated, is presented.

Keywords: keyword, keyword, keyword

Introduction

Up to now the processes within the interface boundary region have been very intensively investigated, because precisely in this region all phase interaction processes (such as epitaxy deposition, surface adsorption, chemical interaction, phase solution and so on), which are responsible for the quality of the layers and devices, produced from them, take place. The molecular beam epitaxy (MBE), the metal-organic chemical vapor deposition (MOCVD) and their new modern modifications such as chemical beam epitaxy (CBE), atomic layer epitaxy (ALE) and so on had proved the possibility to deposit multylayer structures from a great number of very thin layers (with thickness of several angstroms) ensuring very precise control of the composition [ASAI K. et.al.; CASEY H. et.al.; KAUKITU A. et.al.; NOZAWA K. et.al.; OHKOUCHI S. et.al.].

Nevertheless, the liquid phase growth methods are still useful for those devices, where relatively thick layers (more than 0.01 μm) [ANDREEV V.M. et.al; SAKAI S. et.al.] are needed (for example for photocell production, for some types of laser diodes and LED’s). With their structural perfection and their purity the liquid phase epitaxy (LPE) layers are not inferior to the layers, grown by the above mentioned gas phase epitaxy methods. The single crystals growth is always carried out from a liquid phase. All above means that the investigation of the processes, occurring in the phase boundary region between the liquid phase and the solid phase, is very important for obtaining a high quality of the grown material.

Theory

The aim of this paper is to point out some correlations within the interface boundary region during the liquid phase epitaxial growth process, which influence directly the epitaxial layer formation. We will consider the most widely used liquid phase epitaxy methods namely: epitaxy by the linear temperature cooling method and epitaxy by the step cooling method [CASEY H. et.al.; PEEV N.S. Vol. 25, No. 11]. They are used for epitaxy layer deposition of the $A^{III}B^{V}$, $A^{II}B^{VI}$ and their ternary and quaternary compounds. In fact, they are two different

epitaxy layer deposition approaches but in both cases there are some identical features namely:

- supercooling above the crystallization boundary is created by temperature decrease,
- the change of temperature is very slow and the new temperature value is reached simultaneously in the whole volume of the considered system, therefore in the liquid and as well as in the solid phase no temperature gradients appears.

This similarity allows both cases to be considered in parallel.

The case of a n-component solid phase contacting with an own n-component liquid phase ("own" means that at constant temperature both phases are in equilibrium but if a supercooling appears the solid phase grows from the liquid phase). The equilibrium state, at a given process temperature, of the n-component system is determined by the system's liquidus surface while the epitaxy process is determined by the supersaturation above the crystallization boundary – the supersaturation depends on the slope of the liquidus surface at the process temperature.

In the investigated system there are no chemical interactions in the volume of the system and no evaporation takes place. Therefore the system may be considered as a closed system, hence, its mass is constant: $m_o = m^S + m^L = const$ (m_o is the mass of the whole system, m^S is the mass of the solid phase and m^L is the mass of the liquid phase). The same is valid for an arbitrary i^{th} component of the system: $m_{io} = m_i^S + m_i^L = const$.

During the epitaxy layer deposition the mass of each component from the liquid phase will decrease by dm_i^L and the mass of each component of the solid phase will increase by dm_i^S. Due to this the system is closed and both quantities are equal: $\left|dm_i^L\right| = dm_i^S = dm_i$.

From the relation:

$$\frac{dm_i^L / M_i}{g_i} = \frac{dm_j^L / M_j}{g_j} \tag{1}$$

where i and j are arbitrary components of the system, M_i and M_j are their atomic (or molecular) weights and g_i and g_j are the stochiometric coefficients of these components taken from the chemical formula of the growing compound, one may easily obtain the following expression:

$$v_{gr.o} = v_{gr.i} = \frac{M_o}{\gamma_o^S . M_i . g_i} . \frac{dm_i^L}{dt} \tag{2}$$

where the growth rate of the compound $v_{gr.o}$ is shown as a function of the parameters of an arbitrary i^{th} component of the system, γ_o^S is the density of the grown compound [g/cm^3], and $M_o = \sum_{i=1}^{n} g_i . M_i$ is the molecular weight of the compound.

The change of the concentration in the liquid phase of an arbitrary i^{th} component during the growth process performed at a very small temperature decrease is given by the expression:

$$dC_i^L = \frac{C_k^L}{C_k^S} . (C_i^L - C_i^S) . \frac{dm_k^L}{m_k^L} \tag{3}$$

In the last equation the quantity dm_k^L is positive – the "minus sign" means, that the mass decreases with time and a deposition process takes place, but the minus sign was taken into

account during the calculations[1]. This relation gives the change of the total concentration of an arbitrary ith component in the whole volume of the liquid phase not taking into consideration its gradient distribution. The k-component is considered as a basic component and it is not specified - this means that any component in the system may be considered as a basic one.

For different ratio of the quantities C_i^L and C_i^S the behavior of the components during the growth process will be substantially different and they will be deposited on the crystal surface at substantially different conditions [Peev N.S. Vol. 25, No. 6]:

- for $(C_i^L - C_i^S) < 0$ the relations $dC_i^L < 0$, $\partial C_i^L / \partial t < 0$; $\partial C_i^L / \partial x > 0$ are valid – the distribution of the ith component in the liquid phase volume is characterized by a positive concentration gradient and its concentration will always decrease with time (Fig. 1).
- for $(C_j^L - C_j^S) > 0$ the relations $dC_j^L > 0$, $\partial C_j^L / \partial t > 0$; $\partial C_j^L / \partial x < 0$ are valid – the distribution of the jth component in the liquid phase volume is characterized by a negative concentration gradient and its concentration will always increase with time (Fig. 2).

Case of positive concentration gradient

$(\partial C_i^L / \partial x > 0)$

With a positive concentration gradient in the liquid phase the mass flux of the ith -component will occur in the direction towards the interface region (Fig.1) and in this way above the crystallization boundary a supersaturation is always present. The whole volume of the liquid phase is supersaturated relative to the ith - component ($\Delta C_i^L > 0$) and the supersaturation decreases towards the interface and precisely on the substrate surface its value is zero. The temperature decrease leads to decrease of both, the equilibrium concentration $C_{i,eq}^L$ and the true concentration of the component.

This is the classic case of the epitaxy process described in many works and because of this we will not discuss it in greater detail here. At each point of the liquid phase volume the requirement of the mass flow balance must be fulfilled (Fig.1):

$$J_{vi}^L = D_{vi}^L . \frac{\partial N_i^L (x > \Delta)}{\partial x} = J_{Si}^L = D_{Si}^L . \frac{\partial N_i^L (x < \Delta)}{\partial x} = \frac{\gamma_o^S . g_i . \eta}{G_o . M_o} . v_{gr.o} \qquad (4)$$

where $G_o = \sum_{i=1}^{n} g_i$ is the sum of the moles of the components in the growing compound and N_i^L is the atomic concentration [at/cm^3] of the ith - component and η is the Avogadro's number. The other notations used in this work are the same as in (PEEV N.S., Vol.25, No.6) - J_{Si}^L is the flux of the ith-component in the phase boundary region, J_{vi}^L is the flux of the same component in the volume of the liquid phase, Δ is the thickness of the phase boundary region.

The phase in the interface region is structured similar to the solid phase and this means that the diffusion coefficient there (D_{Si}^L) is much smaller than the diffusion coefficient in the

[1] Equation 3 differs from equation 13 of (PEEV N.S., Vol.25, No.6) by a minus sign. In that work the Equation 13 was derived for an enrichment process, when the mass of the components m_k^L increases with time - at time t the mass is m_k^L and at time (t+dt) it is ($m_k^L + dm_k^L$) . Because of that for a deposition process the dm_k^L in equation 13 is with a minus sign (negative). In this work a deposition process is analyzed. The mass of the kth-component at (t+dt) is ($m_k^L - dm_k^L$)- therefore for a deposition process the sign before dm_k^L in equation 3 is positive.

liquid phase volume (D_{vi}^{L}) : $D_{Si}^{L} << D_{vi}^{L}$. Therefore the concentration gradient in the interface region is much greater than that in the liquid phase volume, but at x=0, despite the large gradient, the value of the concentration can not be less than its equilibrium value.

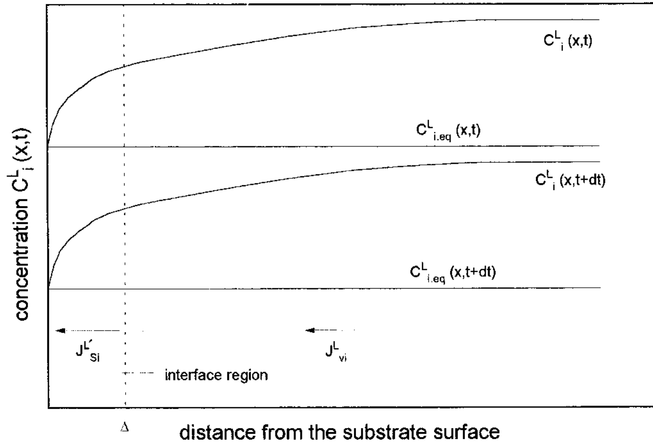

Fig. 1: The distribution of the ith - component in the liquid phase volume and in the phase boundary region with positive concentration gradient.

Case of negative concentration gradient

$(\partial C_j^L / \partial x < 0)$

In this case the concentration of the jth - component close to the interface region is higher than that in the liquid phase volume (Fig. 2) and because of this its mass transport occurs in the direction from the phase boundary region to the liquid phase volume. In general, the liquid phase is superheated relative to jth - component ($\Delta C_j^L < 0$), but this circumstance does not prevent the participation of the jth - component in the growth process (at these conditions the growth of GaAs or $Al_xGa_{1-x}As$ is performed, where the liquid phase is always superheated relative to Ga).

During temperature decrease the equilibrium concentration of the jth -component ($C_{j,eq}^L$) and its true concentration will continually increase. Despite this the mass transport is towards the liquid phase volume, the jth - component will participate in the growth process due to the flux $J_{Sj}^{L'}$, which causes a mass transport towards the crystal surface and which is, obviously, not a diffusion transport. This flux gives the number of the jth - component particles, which for a unit time, are deposited on the unit area of the crystal surface. It is not difficult to show the validity of the following relation:

$$J_{Sj}^{L'} = \frac{\gamma_o^S . g_j . \eta}{G_o . M_o} . v_{gr.o} \tag{5}$$

All other fluxes are directed towards the liquid phase volume (J_{vj}^L is the flux in the volume of the liquid phase and the J_{Sj}^L is the flux in the interface region) and as a consequence this leads to the depletion of the interface region relative to the jth - component. Equation 5 is obtained from equation 2, equation 7 of (PEEV N.S., Vol.25, No.6) and the expression $C_i^S = J_{Si}^{L'} / \sum_{j=1}^{n} J_{Sj}^{L'}$.

Let for time dt the temperature to decrease by about dT = v_T.dt which causes the increase of the equilibrium concentration by about $dC^L_{j.eq} = dT/k_j$, where k_j is the slope of the liquidus surface relative to the jth- component and v_T is the temperature cooling rate. As a rule the temperature cooling rate is very small, hence, the deviation from the equilibrium state of the system is also very small. In this way in the liquid phase volume the jth - component will have the following distribution: in the liquid phase far away from the interface its concentration will be almost equal to the equilibrium value and towards the interface, due to the negative concentration gradient, the concentration of the jth - component will be increase. Summing the fluxes of the jth - component in the liquid phase one obtains:

$$J^L_{Sj} = J^L_{vj} - J^{L'}_{Sj}; \rightarrow D^L_{Sj}.\frac{\partial N^L_{Sj}(x<\Delta)}{\partial x} = D^L_{vj}.\frac{\partial N^L_{vj}(x>\Delta)}{\partial x} + \frac{\gamma^S_o.g_j.\eta}{G_o.M_o}.v_{gr.o} \qquad (6)$$

From equation 6 it follows that the concentration gradient of the jth - component in the interface region will be much greater than that in the liquid phase volume due to the following: **1**. the phase in the interface region is similar, from structural point of view, to the solid phase and this means that the following relations are valid - $D^L_{Sj} << D^L_{vj}; \rightarrow \partial N^L_{Sj}(x< \quad)/\partial x >> \partial N^L_{vj}(x> \quad)/\partial x$; **2**. the flux of the jth - component in the interface region J^L_{Sj} must exceed the flux in the liquid phase volume J^L_{vj} by the value of the non-diffusion flux $J^{L'}_{Sj}$, given by equation 5, which appears as a second term on the right side of equation 6, and is added to J^L_{vj}.

Due to the sharp increase of the jth - component concentration towards the crystal surface, we assume, that at x=δ_j the true concentration C^L_j becomes greater than the equilibrium value of this component. In this way, in a very small region (0, δ_j), close to the crystal surface, there appears supersaturation relative to the jth - component. Because of this supersaturation the jth - component will participate in the growth process.

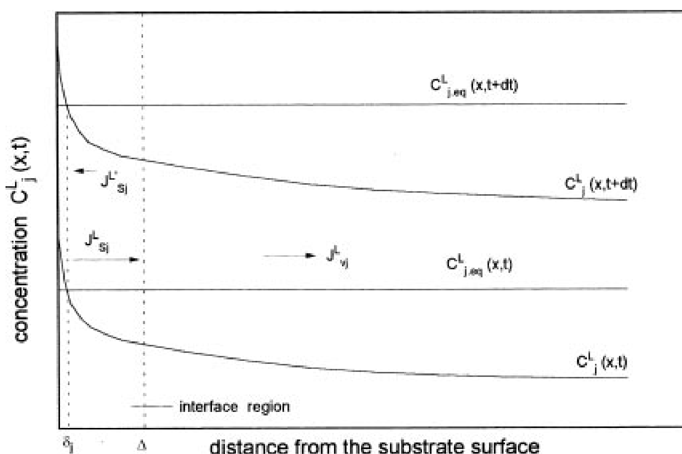

Fig. 2: The distribution of the jth - component in the liquid phase volume and in the phase boundary region with negative concentration gradient.

The case, shown in Fig.2, obviously, differs from the widely spread opinion that the true concentration above the substrate surface coincides with the equilibrium one. In order to point out the presence of supersaturation, relative to the jth - component, we have assumed

that above the substrate surface a supersaturated region (0, δ_j) is present. Now equation 6 may be rewritten – it is obviously valid only in the region (0, δ_j), where the flux $J_{Sj}^{L'}$ is defined, but not in the region (0, Δ). The presence of supersaturation in the region (0, δ_j) explains the meaning of the flux $J_{Sj}^{L'}$ - it is really not a diffusion flux and it is caused by the supersaturation above the crystal surface.

Discussion

Depending on the ratio between the quantities C_i^L and C_i^S the behavior of the components will be substantially different. The deposition of the ith - components at positive value of supersaturation ($\Delta C_i^L > 0$) leads to the decrease of the component mass in the liquid phase (dm_i^L <0) and to reduction of their concentrations (dC_i^L /dt<0) and vice versa the jth - components are deposited at negative value of the supersaturation ($\Delta C_j^L < 0$), their masses also decrease with time (dm_j^L <0), but their concentration increase (dC_j^L /dt>0). Because of the relation $C_i^L < C_i^S$ the relative participation of the ith - components in the epitaxy layer formation is greater than the relative participation of the jth - components ($C_j^L > C_j^S$). The deposition of the masses dm_i^L of the ith - components on the substrate, forming the epitaxy layer, occurs precisely in the interface region and leads:

- to reduction there of the concentration of the ith - components by the value dC_i^L in accordance with equation 3. Because of the near equilibrium conditions the new concentration value must be a point of the system liquidus surface;
- to sharp increase there of the jth - components concentration C_j^L due to the depletion of the interface region relative to ith - components. Because of this above the crystal surface there arises a supersaturation relative to the jth - component. In order to reach the equilibrium state, deposition of the corresponding masses dm_j^L (see equation 1) of the jth-components, is also needed.

The jth - components in practice are usually the solvent materials - in the liquid phase epitaxy of GaAs and $Al_xGa_{1-x}As$ semiconductors it is the Ga component and the doping materials (Te,Sn, Zn) and in the liquid phase epitaxy of SiC it is, for example, Tb, or Dy or other rare earth metals. All other components of the corresponding system are the ith - components - they are As and Al in the LPE of GaAs and $Al_xGa_{1-x}As$ and Si and C in the LPE of SiC.

Up to now we have considered the case of near equilibrium conditions LPE which are observed at very low temperature cooling rate and/or at very low values of the liquid phase thickness (about 1 mm). The thickness of the liquid phase of the system is often of the order of 10 or more mm’s (for example for a crystal growth process) and then substantial deviation from the equilibrium state may be observed.

In the case of a very thick liquid phase and if the graphite boat is situated precisely on the heater axis, during cooling there will arise a temperature maximum in the region of the heater axis - the maximum temperature will be several degrees higher (the value of the temperature difference depends on the cooling rate and on the heater diameter) (Fig.3).

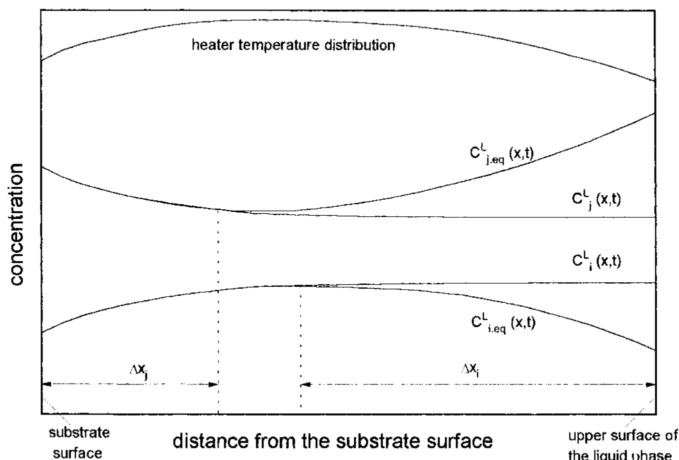

Fig. 3: Arising of supersaturated regions Δx_i and Δx_i in the liquid phase volume far away from the phase boundary in the case of a non-isothermic liquid phase.

Depending on the liquid phase position in the heater and on its thickness a great number of situations are possible – a possible situation is shown on Fig.3. Precisely on the solid state surface the supersaturation is assumed to be zero. The values of the equilibrium concentration follow the temperature distribution in the liquid phase. The true values of the component concentrations depend on the epitaxy growth process and on the diffusion mass transport. In the case of a jth- component the supersaturation may occur not only close to the substrate surface but also in the liquid phase volume far away from the substrate - on Fig.3 this region is denoted by Δx_j. Considering the distribution of a ith- component one may observe that not only the region above the crystallization boundary is supersaturated but the upper surface of the liquid phase is also supersaturated - region Δx_i on Fig.3. The dimensions of these regions depend on the thickness of the liquid phase and on the duration of the cooling process.

If both regions do not overlap (the case from Fig.3) than there are no conditions for a nucleation process. In the case of overlapping of both regions in a region Δx_o a nucleation process in the liquid phase volume will be quite possible. At the beginning the supersaturation (arising in the region Δx_o) is very slow (less than the supersaturation threshold value, needed for the nucleation process) and only a few pre-nuclei will appear. The migration process of the pre-nuclei through the liquid phase volume towards the phase boundaries will occur very slow, with very small values of the diffusion coefficients. In this way, in the volume of the liquid phase a accumulation process of such pre-nuclei will take place. If the growth process requires prolonged cooling (more than 20K – the threshold supersaturation value for the system GaAs-Ga is about 10-15K (Casey H.)) and if the liquid phase is very thick (of about 10-15 mm), then it is quite possible to reach the threshold supersaturation, value which leads to the appearance of three-dimensional nuclei. For the growth process of GaAs the threshold supercooling value is about 10-15 K. The appearance of three-dimensional nuclei in the liquid phase volume, discussed in (Peev N.S., Jour. of Crystal Growth), will significantly influence the epitaxy growth process.

Conclusions

In the present paper the component behavior of an n-component system during the growth process is considered. A part of components are deposited on the substrate in the classic way due to the diffusion mass transport, directed towards the interface region. Precisely above the

substrate there appears a supersaturation and therefore the components are deposited onto it. For other components the diffusion mass transport is directed from the interface region towards the liquid phase volume and, relative to them, the liquid phase is superheated. As a consequence of the large concentration gradient of the above mentioned components in the interface region, the true concentration surpasses the value of the equilibrium concentration and, relative to these components, there arises a supersaturation. Due to this supersaturation these components participate in the growth process, despite this the liquid phase volume, in general, is superheated to these components.

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