1 Introduction to Liquid Phase Epitaxy

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1.1 GENERAL ASPECTS OF LIQUID PHASE EPITAXY

Liquid phase epitaxy (LPE) has been applied to many compounds, but the main applications are compound semiconductors and magnetic rare-earth iron garnets. The electronic, opto-electronic and magneto-optic technologies are based on thin layer- or multilayer structures that are deposited by epitaxial processes onto flat, oriented and single-crystalline substrates. The lifetime and the performance of microelectronic, photonic and magnetic devices are determined by the purity, the structural perfection, the stoichiometry, and the homogeneity of the epitaxial layers (*epilayers*) and by the surface flatness of layers and interfaces. For example, traces of oxygen in GaAs devices reduce their performance, and dislocations have a detrimental effect on threshold voltage of GaAs transistors (Miyazawa *et al.*, 1986) and on the efficiencies of light emitting diodes (LEDs) (Lester *et al.*, 1995).

Liquid phase epitaxy is growth from high-temperature solutions, so that many principles, choice of solvents, and technological experiences from growth of bulk crystals (see Elwell and Scheel, 1975) can be transferred to LPE. The epitaxial deposition can be done from diluted solutions at low temperature, from concentrated solutions at higher temperature and even from melts near the high melting point (Nakajima *et al.*, 2005). In practice, LPE is done mostly from dilute solutions, because this allows firstly to apply lower growth rates for improved thickness control, secondly to apply lower growth temperatures for improved structural perfection and stoichiometry and to reduce the detrimental effects of thermal expansion differences of substrate and epilayer, and thirdly to reduce the risk of unwanted spontaneously nucleated crystallites.

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Here we should introduce the *principle of the single optimum growth technology* (Scheel, 2003): *For a given crystal or epilayer with specified application and desirable device performance, there can be only one single optimum growth technology if one considers thermodynamics, features of growth technologies, economics, timeliness, ecology, etc.*

In silicon and GaAs microelectronics, where submicrometer structures are fabricated in integrated circuits, the epitaxial deposition from the vapor phase is generally applied. Due to the high surface tension of the liquid metallic solutions of semiconductors, such small structures of less than 1 μm cannot yet be fabricated directly by LPE growth. However, LPE has numerous advantages and therefore is the major production technique for LEDs (two-thirds of the worldwide LED production) and for magneto-optic bulk layers. In comparison with epitaxy from the vapor phase, the strengths of LPE are:

- due to near-equilibrium conditions during epitaxial layer deposition the structural perfection of the layers is superior and that quasi-atomically flat surfaces and interfaces can be achieved;
- generally excellent stoichiometry of the layers is obtained;
- due to comparably high solute concentrations relatively high growth rates can be applied;
- LPE in most cases is a very economic epitaxial deposition technique, especially when up-scaled to mass production.

There is justified hope that LPE will become essential for production of quasi-perfect layers of SiC, GaN, AlN, and of high-temperature superconductors, and even GaAs and other substrates may provide LPE surface layers of improved perfection in competition with complex substrate preparation and annealing procedures.

However, there are limitations for LPE with respect to miniaturized structure size (which, however, could be achieved by lithography and etching perfect LPE layers), with respect to immiscible compositions that can not be grown by an equilibrium technique, and with respect to stringent substrate requirements (small misfit, similar thermal expansion coefficient of substrate and layer, and very small misorientation) when atomically flat surfaces and interfaces are to be achieved. Purity is not a problem when constituent elements or compounds are utilized as solvents, for example Ga for LPE of GaAs, the $BaCuO_2$-CuO eutectic as solvent for the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO). In other cases like LPE of magnetic garnets the solvent can be selected according to the criteria discussed in Chapter 3 of Elwell and Scheel (Elwell and Scheel, 1975), or solvent constituents are chosen that are useful for the application like Bi_2O_3 for bismuth substitution in magnetic garnets.

In contrast to the widespread opinion that LPE is an easy, simple and old-fashioned technology, it will be shown that the contrary is the case, when large-area extremely flat layers or superlattices are to be grown. LPE has almost disappeared from universities so that the know-how exists practically only in industries, and because the development of a new layer or multilayer structure by LPE requires 1–3 years, in contrast to popular molecular beam epitaxy (MBE) and metal-organic vapor-phase epitaxy (MOVPE). The two latter methods allow, by using expensive computer-controlled machines, preparation of new layers or superlattice structures within typically 3 months, so that the PhD student can spend the majority of his thesis time on device fabrication and physical measurements.

These facts explain why LPE publications have become scarce, so that this important technology is widely forgotten, it is pushed aside by the 'modern' technologies.

In the following, the various epitaxial growth modes will be discussed and how they appear as functions of interface thermodynamics, thermodynamic driving force (supersaturation), misfit between substrate and epilayer, and substrate misorientation. From this discussion we shall recognize from a theoretical standpoint why atomically flat and thus extremely homogeneous layers of oxides and of most semiconductor compounds can be achieved only by a near-equilibrium technique, by LPE. This discussion will also clarify the complexity and enormous difficulties when epilayers are grown by *heteroepitaxy*, that is the substrate and layer have different composition. But even in *homoepitaxy*, when substrate and layer have the same composition, except for a small dopant concentration, the growth conditions have to be optimized in order to achieve the flat and perfect layers mentioned above.

The technological realization of the theoretically derived parameters can be quite demanding. LPE is growth from solution where step bunching, growth instability and inclusions occur when misfit, substrate misorientation, supersaturation, and hydrodynamics as the main growth parameters are not carefully optimized. Near-equilibrium growth by LPE does not tolerate any deviation from the optimized conditions, a reason why numerous LPE attempts of researchers have failed, why macrosteps, ripples and meniscus lines are observed: detrimental defects that can be prevented by careful selection and preparation of the substrate surface, by the purity of the gas atmosphere, and by the precise adjustment of the growth conditions. In contrast to LPE, epitaxy from the vapor phase is not so critical regarding all these growth parameters. Besides the high-supersaturation effects discussed below, the main problem in vapor phase epitaxy is stoichiometry control of complex compounds like high-temperature superconductors. In LPE, the control of stoichiometry is in general not a problem, because the growth temperature is well below the melting point and below the coexistence (solid solution) range of the compounds, so that automatically layers of excellent stoichiometry are deposited.

1.2 EPITAXIAL GROWTH MODES, GROWTH MECHANISMS AND LAYER THICKNESSES

The layer and surface perfection is determined by the epitaxial growth mode, by the mechanisms of surface nucleation and step propagation. In addition to the three well-known growth modes (Volmer–Weber, Stranski–Krastanov, Frank–Van der Merwe) of Bauer (Bauer, 1958) there are five other distinct growth modes and epitaxial growth mechanisms (Scheel, 1997 and in this chapter) that have been individually described by numerous authors: columnar growth, step flow mode, step bunching, and screw-island or spiral-island growth, and the growth on kinked (rough) surfaces. These eight growth modes are shown in three successive steps of development in Figure 1.1.

The three classical growth modes had been derived thermodynamically from the surface and interfacial free energies with the Frank–Van der Merwe (Frank–Van der Merwe, 1949) mode for dominating the interfacial energy between substrate and epilayer, Volmer–Weber (Volmer–Weber, 1926) for the weakest interfacial energy, and Stranski–Krastanov (Stranski–Krastanov, 1938) as the intermediate case. These three well-known growth modes (Bauer,) are shown in the upper part of Figure 1.1; and they are frequently observed

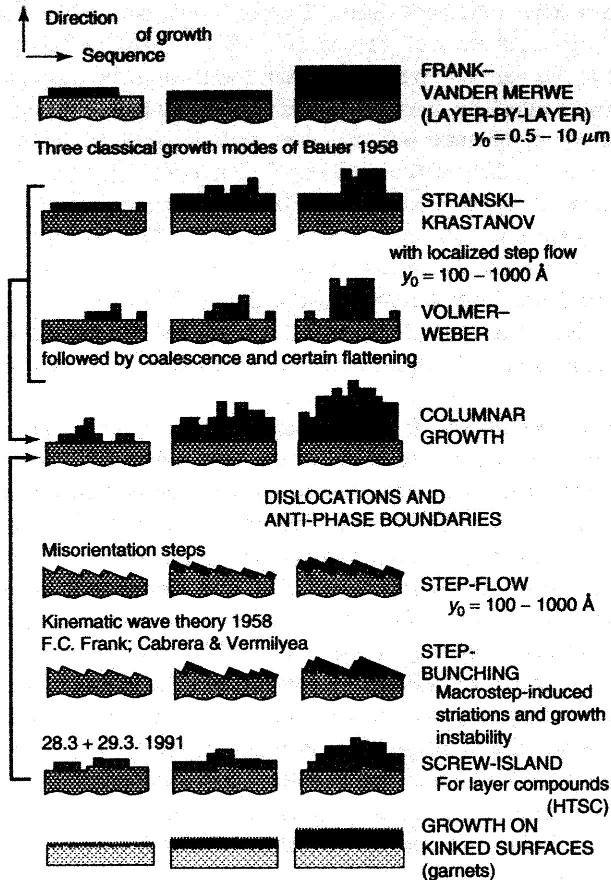

Figure 1.1 Eight epitaxial growth modes. Reprinted from H.J. Scheel, Chapter 28 *Crystal Growth Technology*, editors H.J. Scheel and T. Fukuda, Copyright (2003), with permission from John Wiley & Sons, Ltd

in epitaxial growth. However, different growth modes have been described for the same substrate–epilayer system, thus indicating that growth methods and growth parameters influence the growth modes. Furthermore, the epitaxial growth experience in the past 40 years has given clear evidence of specific growth features that may be described by five distinct and different epitaxial growth modes that are shown in the lower part of Figure 1.1. In the following, first the main experimental parameters determining the appearance of the growth modes will be briefly described followed by the discussion of the growth modes and their impact on layer properties. Other parameters with some influence on the growth mode such as surface diffusion, stoichiometry of deposited compounds, condensing impurities (surfactants), oxidation stage of surface species and partial pressure of reactive species during growth, and surface liquid or surface melting due to impurities (VLS mechanism) or due to partial decomposition, are not yet well understood and will not be discussed here.

The *concentration* of the epilayer-forming species in the growth fluid is very different for vapor phase epitaxy (VPE) and for LPE. For GaAs the solid density of 5.3 g cm^{-3}

is reduced to 0.0065 g cm^{-3} in the vapor, which corresponds to a concentration of $10^{-9}-10^{-6}$ in the vapor depending on working pressure and on dilution by the carrier gas, thus depending on the growth method. In comparison the concentration in LPE is much higher, at 10 % solubility 10^{-1}. In growth from the vapor generally the material flux (in number of species cm^{-2} s^{-1}) is the rate-determining factor for growth. In LPE it is the mass transport through the diffusion boundary layer δ that at a given supersaturation limits the growth rate according to (Nernst, 1904):

$$v = (n - n_e)D/\rho\delta$$

where D is the diffusion coefficient, n the effective concentration or vapor pressure, n_e the equilibrium concentration or vapor pressure, and ρ the density of the crystal. However, with increasing *supersaturation* and growth rate we observe successively step bunching, wavy macrosteps, formation of inclusions, edge nucleation and surface dendrites, hopper growth and bulk dendrites in the transition from stable growth to growth instability. There is a *maximum stable growth rate* v_{max} that is defined as the highest growth rate without growth instability. This was derived from an empirical boundary-layer concept of Carlson (Carlson, 1958) by Scheel and Elwell (Scheel and Elwell, 1972) as a function of the solution flow rate u, the Schmidt number $Sc = \eta/\rho_l D$ with η the dynamic viscosity and ρ_l the density of the liquid, σ the relative supersaturation $(n - n_e)/n_e$, and L the crystal size or substrate diameter, as

$$v_{max} = \{0.214\ D\ u\sigma^2 n_e^2/Sc^{1/3}\rho^2 L\}^{1/2}$$

see also Chapter 6 in Elwell and Scheel (Elwell and Scheel, 1975). This approach, in combination with the faceting transition concept described further below, is essential to achieve flat LPE epilayers. In VPE the supersaturation ratio α of the actual pressure divided by the equilibrium pressure p/p_e qualitatively describes the decreasing supersaturation with increasing substrate temperature, but can often not be used for quantitative interpretation of growth phenomena. Stringfellow (Stringfellow, 1991) has derived the thermodynamic driving forces of epitaxial processes from the free energy differences between the reactants before growth and the crystalline product. For GaAs and growth temperature 1000 K this comparison of the epitaxial driving forces is shown in Figure 1.2.

One can recognize that the supersaturations in epitaxy from the vapor phase are orders of magnitude higher than in LPE where the supersaturation can be adjusted to a negative value for etching, exactly at zero for thermodynamic equilibrium, and at small positive values suitable for stable and economic growth rates to achieve atomically flat surfaces (Scheel, 1980; Chernov and Scheel, 1995). The free energy differences of Figure 1.2 give only an order of magnitude estimate of the supersaturation. The effective supersaturation during growth can be derived from the surface morphology of as-grown surfaces (Scheel, 1994). The distances y_0 between steps are related to the radius r_S^* of the critical two-dimensional nucleus as elaborated by Cabrera and Levine (Cabrera and Levine 1956):

$$y_0 = 19\ r_S^* = 19\ \gamma_m V_m/a^2 RT\sigma$$

with γ_m the energy per growth unit, V_m the molar volume, and a the size of the growth unit.

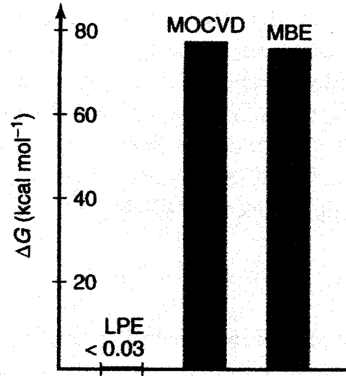

Figure 1.2 Gibbs free energy differences between reactants and products (layers, crystals). The estimated thermodynamic driving forces for LPE ($\Delta T < 6$ K), MOCVD (TMGa + arsine) and MBE (Ga + As_4) of GaAs at 1000 K. (After Stringfellow, 1991) Reprinted from *J. Cryst. Growth*, **115**, Stringfellow, 1, Copyright (1991), with permission from Elsevier

Table 1.1 shows that from typically observed interstep distances for VPE and for LPE for the examples GaAs and the high-temperature superconductor (HTSC) YBCO the supersaturation is about 60 times lower in LPE of GaAs and 200 times lower in LPE of YBCO. This explains the different growth modes for VPE and LPE as shown below.

For HTSCs the measured interstep distances increased with the substrate temperatures as expected (Nishinaga and Scheel, 1996), but due to the thermodynamic stability limits of HTSC compounds the temperature can not be raised sufficiently to achieve interstep distances comparable with LPE.

In heteroepitaxy the *lattice mismatch* between substrate and epilayer at the growth temperature has a significant effect on nucleation behavior and the epitaxial growth mode and thus on the structural perfection of the layer, and the *thermal expansion difference* between the substrate and film may further deteriorate the layer perfection or may cause cracking upon cooling to room temperature. The lattice mismatch or *misfit* f is defined as the relative difference of the lattice spacings of the substrate a_S and of the film a_F : $f = (a_S - a_F)/a_F$. During layer deposition the misfit is first accommodated by a homogeneous strain, and after reaching a critical layer thickness, which depends on the degree of misfit, *misfit dislocations* are formed that are characterized by a periodical elastic strain with a period equal to the dislocation spacing (Van der Merwe, 1973). At small misfit, for instance

Table 1.1 Supersaturation ratios for VPE and LPE derived from interstep distances y_0 of GaAs and of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO)

	For GaAs		For YBCO	
	MBE, MOVPE	LPE	VPE, MOVPE	LPE
y_0	20–100 nm	6 μm	14–30 nm	6 μm (0.6–17 μm)
r_S^*	1.1–5.5 nm	300 nm	0.8–1.6 nm	300 nm
	$\sigma_{MBE,MOVPE} \sim 60 \times \sigma_{LPE}$			$\sigma_{VPE,MOVPE} \sim 200 \times \sigma_{LPE}$

by epitaxial growth of a doped layer onto an undoped substrate, the formation of misfit dislocations is prevented, but the substrate–layer structure may become bent due to the misfit strain. The curvature can be used, when only one side of the substrate is epitaxially overgrown, to monitor the layer thickness during the growth process by laser reflection.

The *misorientation* of the substrate, i.e. the deviation angle from the ideal crystallographic plane, provides misorientation steps of which the distance is determined by the misorientation angle and by the lattice constants. This interstep distance can be made so small that the formation of nuclei and growth islands can be suppressed resulting in a pure step-flow mode.

The growth on kinked or atomically rough surfaces and on stepped surfaces possible at special crystal orientations, for example in growth of garnet layers, the non-equilibrium surfaces provide kink sites on to which the species can be attached, practically with negligible surface diffusion and without step propagation.

In the following, the seven epitaxial growth modes shown in Figure 1.1 will be described along with features allowing clear distinction that is necessary due to the misuse of layer-by-layer growth for step-flow mode, for example.

In the *layer-by-layer* or *Frank–Van der Merwe* (Frank and van der Merwe, 1949) *growth mode* (F–VM mode) steps with large interstep distances, typically more than 1 μm, propagate over macroscopic distances. In the case of perfect crystal surfaces, the supersaturation increases until surface nucleation occurs and the steps move to the edge of the crystal until the formation of the monolayer is completed. Then the supersaturation rises again for surface nucleation and the formation of the next monolayer. Normally, however, there are continuous step sources like screw dislocations or other defects, so that the layer-by-layer mechanism works continuously and spreads layers at large interstep distances over macroscopic distances. Screw dislocations may cause the spiral growth mechanism (described by the BCF theory; Burton *et al.*, 1951) that may lead to shallow growth hillocks with very small slopes, depending on supersaturation these can be seconds to minutes of arc. At the hillock boundaries the steps arriving from neighboring hillocks are annihilated and thus may cause screw dislocations or other defects. Thus, the hillock boundaries may cause local strain fields and variation of the incorporation rates of impurities and dopants, or the local strain may getter or reject impurities during annealing processes. This inhomogeneity may be suppressed by providing one single step source or by using substrates of well-defined small misorientation that corresponds to the interstep distance from the applied supersaturation. The F–VM growth mode and such perfect and homogeneous layers can only be achieved by LPE or by VPE at very high growth temperatures (e.g. in silicon epitaxy above 1100 °C interstep distances above 1 μm can be observed). For compound semiconductors and most oxide compounds with thermodynamic stability limits only LPE at low supersaturation can yield atomically flat surfaces.

The *Volmer–Weber (Volmer and Weber, 1926) growth mode* (V–W mode) is typical of VPE where a large number of surface nuclei (typically $10^6 - 10^{11}\ \mathrm{cm^{-2}}$) and growth islands are formed due to the high supersaturation described above. This initial phase is followed by spreading,[1] that is by localized step flow and growth of three-dimensional islands, and finally by coalescence to a compact layer. The supersaturation effect can be dominating so that even in homoepitaxy the V–W mode is observed, for example in HTSC oxide compounds (Konishi *et al.*, 1994). Continued growth of a layer first initiated

[1] Theorists like to call this the birth-and-spread mode.

by the V–W mode often shows *columnar growth* unless there is a healing procedure to enhance surface diffusion, for instance by growth interruption in MBE or by an annealing phase. Columnar growth is a common feature in epitaxy of GaN, diamond, and HTSCs due to their thermodynamic stability limits not allowing a sufficient high growth temperature for reduced supersaturation and effective surface diffusivity and thus healing, see for example the Akasaki–Amano group with columnar growth of GaN on AlN buffer layers (Hiramatsu *et al.*, 1991).

The *Stranski–Krastanov* (Stranski and Krastanov, 1938) *mode* (S–K mode) can be regarded as intermediate between the F–VM and V–W modes. Due to relatively large substrate–epilayer interface energy, first one or two compact monolayers are formed onto which by surface nucleation, analogous to the V–W mode and due to misfit, three-dimensional islands are formed that eventually coalesce to compact layers. As an example, the S–K mode has been demonstrated by MBE growth of InAs onto GaAs substrates (Nabetani *et al.*, 1993).

The detrimental coalescence effects of V–W and S–K films can be suppressed by using substrates of precisely adjusted misorientation (typically 0.8 – 2.5°), so that from the short interstep distances the formation of islands can be prevented and the pure *step-flow mode* achieved. The advantage of this mode has been more and more recognized and has improved structural perfection of vapor-grown layers and device performance. In LPE the application of misoriented substrates limits the applicable supersaturation in order to prevent step bunching and surface corrugations. *Localized step flow* is frequently observed in films growing by the V–W or S–K mode with interstep distances of less than 50 nm. These steps are frequently misinterpreted as layer-by-layer growth, a term that should be reserved to interstep distances of more than 1 μm and step propagation over macroscopic distances by the F–VM mode.

In LPE, frequently *step bunching* is observed when at high supersaturation a high density of steps moves with large step velocities over the surface. By fluctuations, higher steps catch up with lower steps and then move together as double, triple, or in general as macrosteps. The theory of this traffic flow problem by Lighthill and Whitham (Lighthill and Whitham, 1955) was applied in 1958 by Cabrera and Vermilyea (Cabrera and Vermilyea, 1958) and independently by Frank (Frank, 1958) to step bunching (kinematic wave theory). The macrostep-terrace (or thread-riser) morphology causes different incorporation rates of impurities and dopants due to locally varying growth velocities that lead to *macrostep-induced striations* (Scheel, 2003). These striations were observed in cross-sections of LPE-grown layers by etching or by photoluminescence for example by Kajimura *et al.* (Kajimura *et al.*, 1977), Nishizawa *et al.* (Nishizawa *et al.*, 1986) (Figure 1.3) and by Nishinaga *et al.* (Nishinaga *et al.*, 1989). The upper part of Figure 1.3 shows the topview of a LPE-grown GaP layer with three macrosteps which correspond to the surface steps shown in the cross section in the lower part of the Figure One can follow the development and broadening of the macrosteps from smaller steps in the etched layer. The opposite, the removal of macrosteps, can be seen with two examples in Figure 1.4. A Nomarski photograph of an angle-lapped and etched 15-layer structure of n- and p- GaAs grown by a slider-free LPE technology (Scheel 1977) is shown in Figure 1.4a. The first 6 layers show macrosteps and their traces in the etched p-GaAs layers until with layer 7 the transition to the facet starts on the left side. With layer 12 and total growth of about 25 μm the faceting transition is complete in this case where the substrate misorientation was 0.165 degrees. Figure 1.4b shows an example where the

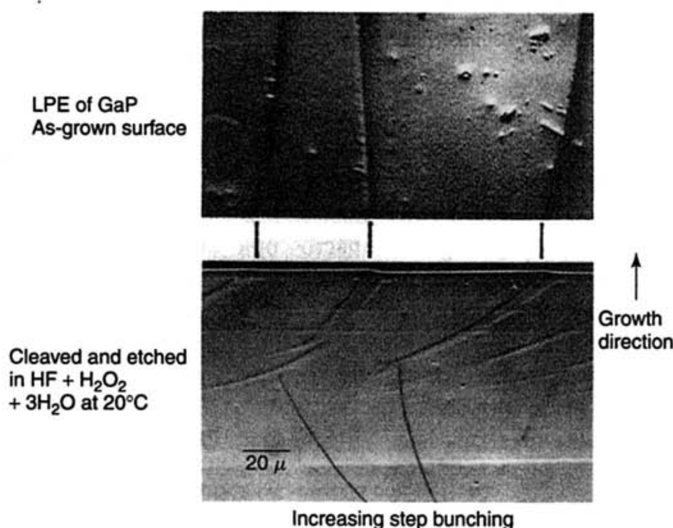

Figure 1.3 Macrostep-induced striations. Reprinted with permission from *Proc. 2nd Int. School on Semiconductor Optoelectronics*, J. Nishizawa and Y. Okuno, Cetniewo, Poland, 1978

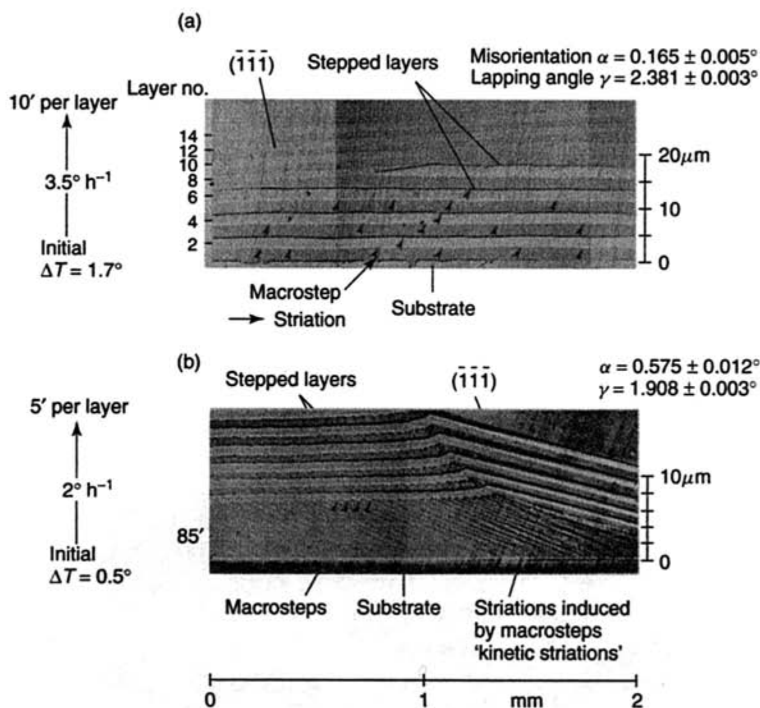

Figure 1.4 Transition to faceting in LPE. Reprinted from *Appl. Phys. Lett.*, Transition to faceting in multilayer liquid phase epitaxy of GaAs, **37**, Scheel, 70–73, Copyright (1980), with permission from American Institute of Physics

transition to the facet was only partially successful due to the large substrate misorientation angle of nearly 0.6 degrees.The facet started on the right side and covers after 15 μm growth nearly half of the photographed surface. The macrosteps and the corresponding striations can be clearly recognized on the left facet-free side. These experimental results (Scheel 1980) were analyzed theoretically by Chernov and Scheel (1995) who showed that by applying a low supersaturation and substrates of small misorientation, step bunching can be suppressed by the transition to faceting, to a growth surface with mono- or double-steps propagating over macroscopic dimensions in the F–VM mode. The resulting quasi-atomically flat surface was proven in the first investigation of an epitaxial surface by scanning-tunneling microscopy by Scheel, Binnig and Rohrer 1982 that showed step heights of 0.65 nm (Figure 1.5), and interstep distances of 6 μm were visible by optical Nomarski interference contrast microscopy (Figure1.6).

LPE on the kinked {111} surface of garnet, a nonequilibrium rough surface, has been developed for the growth of garnet layers for magnetic bubble-domain devices based on

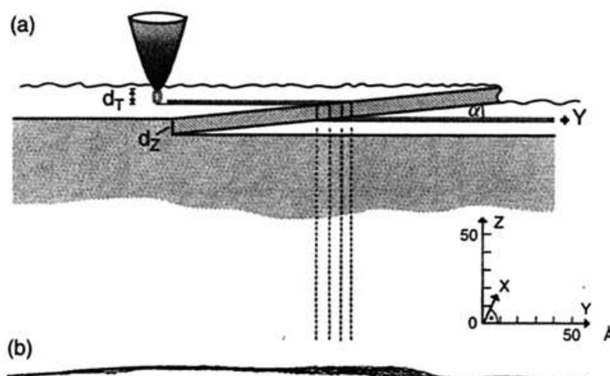

Figure 1.5 Step height by STM. Reprinted from *J. Cryst. Growth*, **60**, Scheel *et al.*, 199, Copyright (1982), with permission from Elsevier

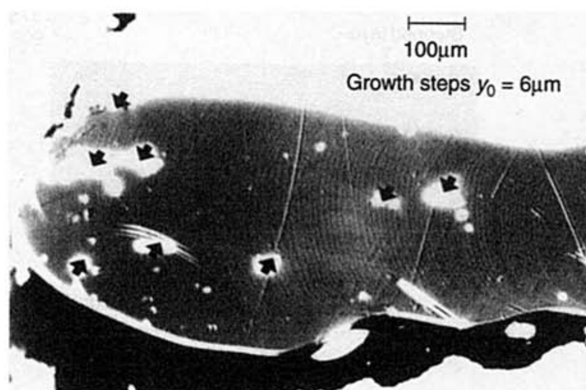

Figure 1.6 Differential interference contrast microscopy (Nomarski) of facet surface. Nomarski step distances of 6 μm are visible. Reprinted from *J. Cryst. Growth*, **60**, Scheel *et al.*, 199, Copyright (1982), with permission from Elsevier

crystallization studies of garnet spheres by Tolksdörf *et al.* (Tolksdorf *et al.*, 1972) and later for bulk magneto-optical layers of millimeter thickness, whereby special care had to be taken with substrate preparation, supersaturation and solvent composition (Hibiya 1983), and thermal symmetry/hydrodynamic growth conditions for the growth surface to remain flat and to prevent the formation of {211} facets (Iino, 2005).

The *screw-island mode* was discovered in STM investigations of the HTSC YBCO grown by sputter deposition and by MOVPE first by Hawley *et al.* (Hawley *et al.*, 1991) and then by Gerber *et al.* (Gerber *et al.*, 1991), who found a high density of screw islands (or spiral islands). The density of these islands corresponds to the density of initially nucleated islands ($10^8 - 10^9$ cm^{-2}) and is dependent on the misorientation of the substrate, so that Scheel (Scheel, 1994) suggested the coalescence of slightly misoriented islands responsible for the formation of screw dislocations with large Burgers vector and thus for the screw-island growth mode. The misorientation angle of the first-formed islands is related to the misfit.

Continuous growth by the screw-island mode leads to coalescence and to columnar growth whereby the number of islands may be reduced at low supersaturation and at high growth temperatures.

For compounds of limited thermodynamic stability or with volatile constituents like GaAs, GaN, SiC, and the HTSC compounds, the appearance of the growth modes is largely predetermined by the choice of the growth method due to the inherent high supersaturations in epitaxy from the vapor phase and the adjustable low supersaturation in LPE. This is demonstrated in Figure 1.7 where the critical radius of the nuclei and the interstep distances are shown as functions of the supersaturation along with typical regions of the epitaxial methods. We can recognize that in LPE the desirable F–VM growth mode can be achieved at low supersaturation and low substrate misfit, whereas a high thermodynamic driving force leads to step bunching. Also misfit, requiring a higher supersaturation for growth, will lead to step bunching and in extreme cases even to V–W or S–K mode that are the typical growth modes for epitaxy from the vapor phase.

For the control of the growth mode, with the goal of achieving the best device performance, the misfit plays an important role, and therefore the use of low-misfit substrates is essential as will be discussed further below. The F–VM growth mode can only be obtained at quasi-zero misfit as can be established from thermodynamic considerations (Van der Merwe, 1979) and as was demonstrated by atomistic simulations using the Lennard–Jones potential (Grabow and Gilmer, 1988). The combined effect of supersaturation and misfit is shown in Figure 1.8, along with the epitaxial methods and the growth modes.

Only in the small corner at low supersaturation and nearly zero misfit can the layer-by-layer growth mode be realized and used to produce low dislocation layers for ultimate device performance, as was early demonstrated with the highest brilliance red LED, and clear green LEDs and many other optoelectronic devices (Nishizawa and Suto, 1994) grown by near-equilibrium LPE. For the example of LEDs the dependence of the efficiency of light output on the structural perfection, i.e. on the dislocation density, was demonstrated in a systematic study of Lester *et al.* (Lester *et al.*, 1995 who collected data of several III-V compound systems. Meanwhile, it has become clear that also for LEDs based on GaN and its alloys, a low dislocation density is important for the brightness.

Homoepitaxial LPE may become important when extremely perfect, quasi-dislocation-free surfaces will be needed for ultimate performance of electronic, optoelectronic, optical

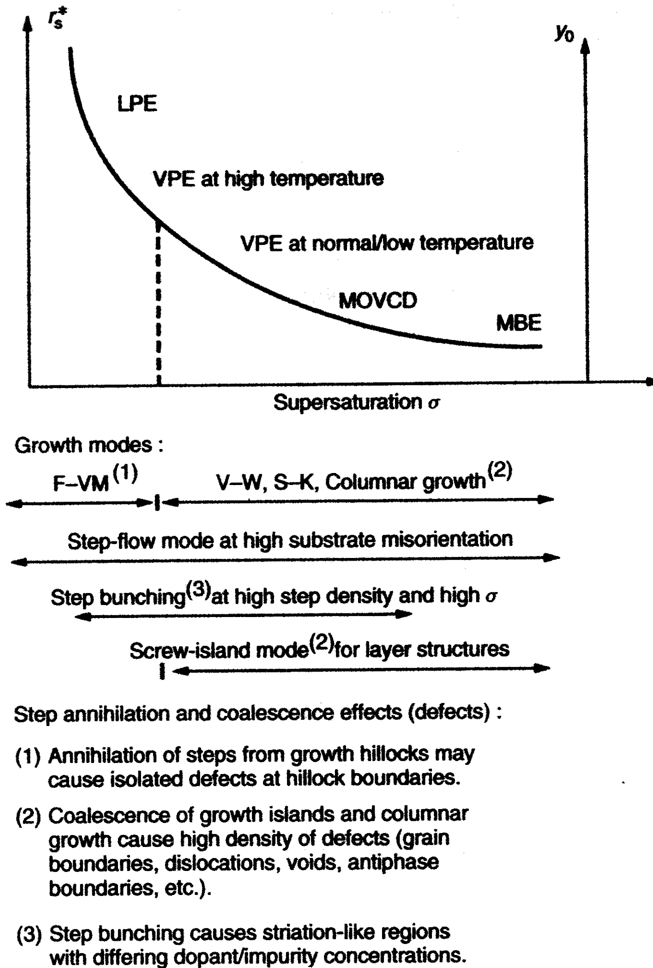

Figure 1.7 Supersaturation versus step distance and epitaxy method. Reprinted from *Crystal Growth Technology*, editors H.J. Scheel and T. Fukuda, Copyright (2003), with permission from John Wiley & Sons, Ltd

and HTSC devices, and when the preparation of correspondingly perfect substrates can not be achieved, or when the preparation of perfect substrate surfaces is too difficult. Besides GaAs one should mention SiC and GaN substrates that when prepared from the vapor phase contain of the order of 10 pipe defects and 10^{10} dislocations cm^{-2}, respectively. By LPE onto GaN (Klemenz and Scheel, 2000) and onto SiC (Ujihara *et al.*, 2005) the defects could be 'overgrown' and surfaces of improved perfection achieved.

The *thickness of LPE grown layers* depends on the growth method like dipping, tipping, tilting and the kind of applied supersaturation (step-cooling, cooling rate or supersaturated solution) and hydrodynamics as discussed by Tiller and Kang (Tiller and Kang, 1968), Minden (Minden, 1970), Mitsuhata (Mitsuhata, 1970), Crossley and Small (Crossley and Small, 1971), Ghez and Lew (Ghez and Lew, 1973), Hsieh (Hsieh, 1974), and Knight

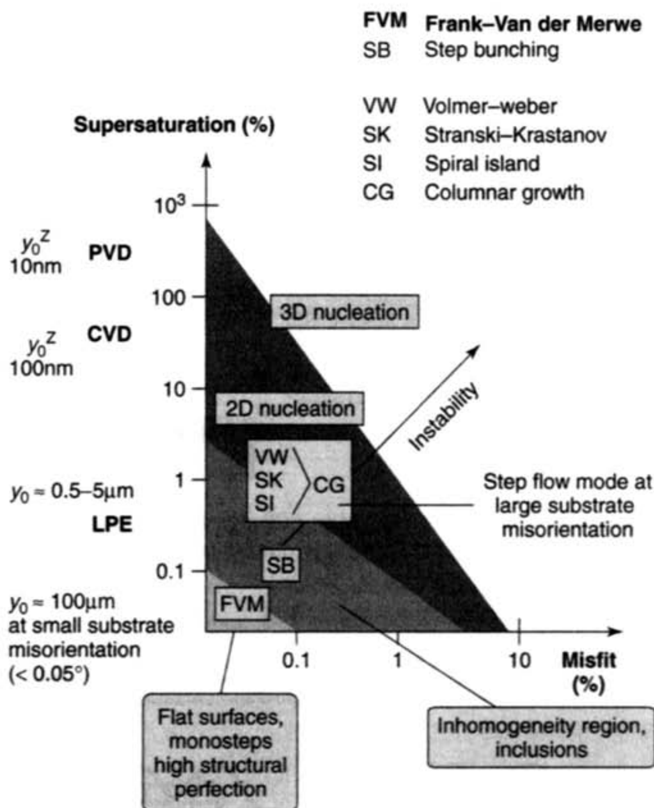

Figure 1.8 Supersaturation, misfit and growth modes. Reprinted from *Crystal Growth Technology*, editors H.J. Scheel and T. Fukuda, Copyright (2003), with permission from John Wiley & Sons, Ltd

et al. (Knight *et al.*, 1974). In LPE of semiconductors the slider technique has been most widely applied, even up to production scale, although it has severe disadvantages as shown in Figure 1.9.

The main disadvantages are scratching of the grown layers and the limitation of total layer or multilayer thickness. A slider-free LPE growth system for semiconductor multilayers and superlattices has been developed ('MultiLPE'; Scheel, 1977) that allowed the transition to faceting and atomically flat surfaces, as discussed above to be achieved, and that in a different topology can be used for *large-scale production of epitaxial multilayers* (Scheel 1975) in a quasi-continuous process (Figure 1.10).

Here a batch of substrates held in an open frame is inserted into the solution that is supersaturated by slow cooling, whereby oscillation about the axis leads to stirring and improves the homogeneity of the melt. By combined rotation and translation of the central axis the batch of substrates is introduced into the next solution, and so on. On both sides of the furnace there are gloveboxes where the substrate batches are mounted and on the other side of the furnace demounted. In the case of GaAs a low oxygen partial pressure, as derived from thermodynamics of oxide formation/Ellingham diagram, is required for the gas atmosphere in order to prevent surface oxidation (scum formation) of the Ga melt

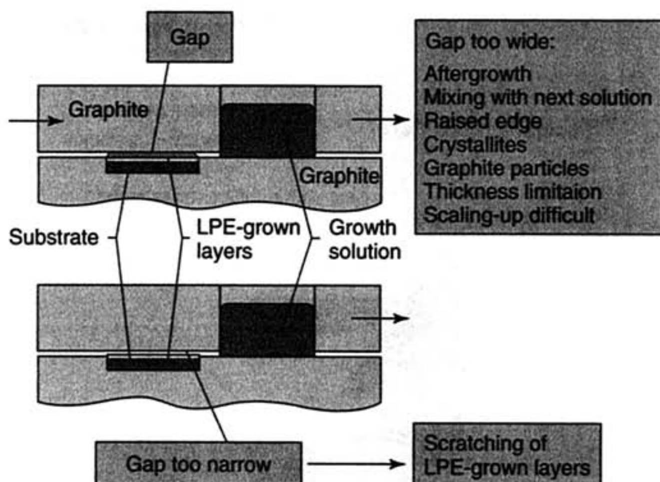

Figure 1.9 Problems with GaAs slider method in LPE. Reprinted from *Crystal Growth Technology*, editors H.J. Scheel and T. Fukuda, Copyright (2003), with permission from John Wiley & Sons, Ltd

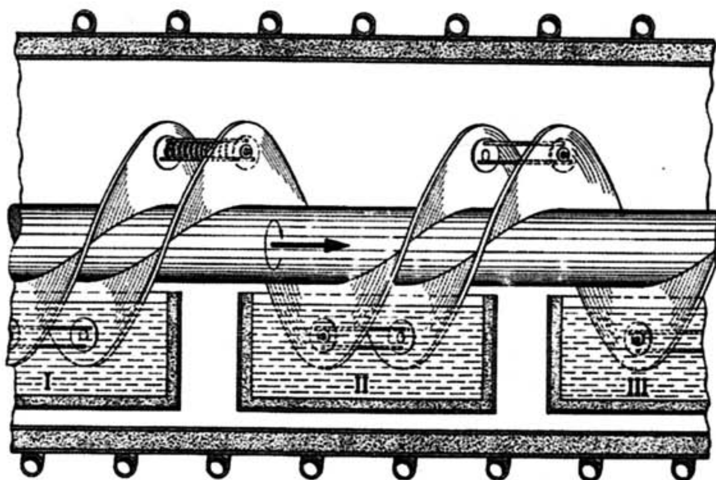

Figure 1.10 LPE mass production by slider-free technology (Scheel 1975)

that causes wetting of the substrate and thus remaining melt fraction that mixes with the next melt/solution.

For LPE of garnet layers the dipping of rotating substrates (Scheel and Schulz-Dubois, 1972) has become widely used. This has the advantage of an adjustable continuous flow towards the rotating disc that was analyzed by Cochran (Cochran 1934) and then applied to the segregation analysis of Czochralski growth by Burton *et al.* (Burton *et al.*, 1953). The resulting quasi-constant hydrodynamic and diffusion boundary layers facilitate the theoretical analysis (Ghez and Giess, 1974), and the stirring action leads to homogenization of the growth solution and an approach to thermodynamic equilibrium, in contrast

to unstirred solutions where high supersaturations may hamper reproducibility and layer homogeneity.

In LPE growth of bulk garnet layers from stirred solutions, steady state is reached soon after inserting the substrates so that the growth rate is automatically given by the volume of the solution and the total surface area of the substrate(s) that has to accept the material that has to precipitate as a function of the solubility curve and the cooling rate. This should allow high reproducibility to be achieved in bulk oxide layer thickness in the case of rotating substrates, especially for oscillatory rotation.

1.3 THE SUBSTRATE PROBLEM

Successful LPE relies on uniform, clean and damage-free substrates with zero or very low dislocation densities. The surfaces should be free from dust, grease, and pits or scratches from the polishing process, and the structural damage from crystal sawing (microcracks, strain) should be removed by a final etching stage. Even commercially available 'epi-ready' substrates should be characterized before use. Normally, the final substrate-preparation stages and the characterization of substrates for LPE are done in clean rooms, depending on the application in class 1000 or class 100 atmosphere. In special cases the meltback of the substrate followed by homoepitaxial regrowth, as proposed by Robertson *et al.* (Robertson *et al.*, 1973), may yield perfect surfaces for following heteroepitaxial LPE growth of the functional layer.

As we have seen above, the orientation, and respectively, the misorientation, of the substrate plays a decisive role in the control of the growth mode and thus in the layer perfection. The required precision of the misorientation angle can be estimated theoretically and taken into account in the crystal sawing, lapping and polishing steps. For the achievement of atomically flat LPE-grown surfaces the misorientation angle should be less than 0.05° (Chernov and Scheel, 1995), which requires a corresponding precision in the crystal-machining steps.

The largest challenge in LPE in the case of heteroepitaxy are the misfit between substrate and epilayer at the growth temperature and the difference of the thermal expansion coefficients.

This problem received much attention during the development of magnetic bubble-domain devices based on garnets during the period 1969–1976, and was approached from both sides, from solid-solution compositions of the layer fitting to the $Gd_3\,Ga_5O_{12}$ (GGG) substrates, and to solid solution substrates fitting to layers with optimum device performance. Thereby the lattice parameters of the mixed garnets can be calculated from published values (Geller, 1967; Winkler *et al.*, 1972) of the end-member garnets using Vegard's rule. The different thermal expansion coefficients of GGG substrate ($\alpha = 9.18 \times 10^{-6}\,°C^{-1}$) and $Y_3Fe_5O_{12}$ (YIG) magnetic garnet fim ($\alpha = 10.35 \times 10^{-6}\,°C^{-1}$) measured by Geller *et al.* (Geller *et al.*, 1969) leads to tensile stress when films that fit a substrate at growth temperature are cooled to room temperature. The stress in an epitaxial film is given (Besser *et al.*, 1972; Carruthers, 1972) by:

$$\sigma_F = \frac{E}{1-\mu}(1-\eta)\left(\frac{a_S - a_F}{a_F}\right) + \eta(\alpha_S - \alpha_F)\Delta T$$

where E is the Young's modulus, μ is the Poisson's ratio of the film, a_S and a_F are the room temperature lattice parameters of substrate and film, respectively, α_S and α_F their thermal expansion coefficients, ΔT the difference between growth and ambient temperatures, and η the fractional stress relief.

The unstrained lattice mismatch $\Delta a = a_S - a_F$ should be within the limits +0.001 nm (tension) and −0.002 nm (compression) according to Besser *et al.* (Besser *et al.*, 1972), Blank and Nielsen (Blank and Nielsen, 1972) and Tolksdorf *et al.* (Tolksdorf *et al.*, 1972) for VPE- and LPE-grown layers. The tensile stress limit of garnet films can be explained in terms of Griffith's (Griffith, 1920) crack theory that predicts an increasing stress limit with decreasing film thickness (Matthews and Klokholm, 1972). The origin, magnitude and configuration of heteroepitaxial stresses in thin oxide films has been reviewed by Carruthers (Carruthers, 1972). The rapid growth direction of pulled gallium garnet substrate crystals is [111], which is fortunately the preferred orientation of the magnetic garnet layers. In GGG crystal pulling relatively high crystal rotation rates are applied in order to achieve a planar growth interface and to prevent {211} facets. However, a compromise has to be found between the core effect, a central strained region in Czochralski-grown crystals, and the formation of striations.

In epitaxy of compound semiconductors there was for a long time the limitation to simple compound substrates like GaAs, GaP, InP, GaSb, CdTe which narrowed the solid solution ranges of layers and thus the bandgap and wavelength ranges for optoelectronic devices.

Only recently has the commercial production of CdHgTe (Capper *et al.*, 2005) and of GaInSb (Dutta, 2005) been achieved by vertical Bridgman growth with the accelerated crucible rotation technique (ACRT), and promising results have also been obtained for the InGaAs (Nishijima *et al.*, 2005) and SiGe (Nakajima *et al.*, 2002) systems. For the Si-Ge system an optical *in situ* monitoring system of the crystal-melt interface allowed the study and optimization of the solidification of the solid solution crystal (Sazaki *et al.*, 2002).

1.4 CONCLUSIONS

LPE is the most powerful epitaxial method to achieve layers and multilayers with the highest structural perfection, best stoichiometry, and with atomically flat surfaces and interfaces. Thus, LPE is most important when ultimate performance of optoelectronic, optical, magnetic, magneto-optic and superconducting devices is envisaged. Future progress is expected when solid-solution substrates become available and then allow the preparation of layers that so far could only be grown by nonequilibrium VPE. However, epitaxy from the vapor phase like MBE and MOVPE is and will remain essential for research when novel layer structures are to be developed in a short time, and for fabrication of devices and integrated structures that can not be made by LPE as the near-equilibrium growth method. On the other hand, there is no fundamental problem to achieve extremely thin layers, even monolayers and superlattices, by LPE, as this is a technological problem that can and will be solved. LPE is the major fabrication method for LEDs and for magneto-optic layers, and it is expected that it will become even more dominant, for instance for the highest efficiency photovoltaic solar cells, when its potential is increasingly recognized. This will be the case when education of epitaxy engineers and epitaxy scientists is established who know thermodynamics and the principles of all epitaxial methods, but

also spread-sheet process analysis, so that they can apply the single optimum economic epitaxial process for their specific epitaxial layer and device requirement. Such multidisciplinary education is urgently needed in order to save resources that are spent when nonoptimal or nonuseful methods are applied for example in HTSCs, where only by LPE the surface flatness required for reliable Josephson/SQUID technology can be expected. Such specialized education is necessary because of the complexity and multidisciplinary nature of crystal and epitaxial growth technology where multiple growth parameters have to be optimized and compromised, and where the substrate problem can be mastered.

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