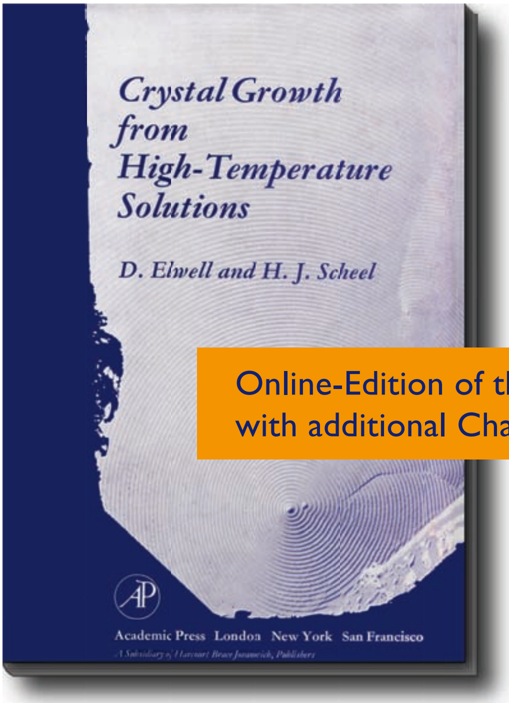

Online-Edition of the original book
with additional Chapter 11 and Appendices A and B

Part 016

Appendix B

Epitaxy and the importance of LPE

In epitaxial growth the mode of nucleation and crystallization is strongly dependent on the bonding between the substrate and the deposited film. Bauer (1958) defined three modes of growth depending upon the surface and interfacial free energies: the **Frank-van der Merwe (FVM) layer-by-layer growth, Volmer-Weber (VW) island growth,** and the **Stranski-Krastanov (SK) growth mode.** In the FVM mode, a new layer is nucleated after the completion of the previous layer. Screw dislocations often act as the nucleation sites for steps, which are typically more than 0.1 μm apart and propagate over macroscopic distances. This mode of growth results in the flattest, most perfect surfaces and is only possible at relatively low supersaturation and either in homoepitaxy, or in heteroepitaxy if there is a good match between the film and the substrate. At high supersaturation, step bunching occurs and the regime is best considered as a departure from the FVM mode.

In the VW growth mode, two-dimensional nucleation occurs over the surface, creating islands of growth which grow laterally and normal to the surface to coalesce into the film. This mode is sometimes referred to as **the birth and spread growth mode.** In this mode, nucleation of a new island occurs before growth of the previous layer is completed. The SK mode is intermediate between the FVM and VW modes, and is characterized by the nucleation of islands after an initial growth of one or two compact layers, with later coalescence into a continuous film.

More recently a mode of epitaxial growth was recognized in which the nucleation occurs in the VW or SK mode, but dislocations are readily generated by the accommodation of small translational or rotational displacements as adjacent islands agglomerate (Scheel 2003&2004). This is referred to as the **Screw-island** or **Spiral-island (SI) growth mode.** If the distance between two-dimensional (2D) nuclei is about 500 Angstroms, the density of nuclei is on the order of $5 \times 10^{10}/cm^2$. A dislocation density of this order of magnitude is often observed in growth from the vapor phase, so this mode of growth is quite common in PVD (physical vapor deposition) and CVD (chemical vapor deposition) especially of heteroepitaxial films of layer compounds like the high-temperature superconductors.

In continuous layer growth by vapor phase epitaxy, the initial growth of a thin layer by the SK, VW or SI growth mode may be followed by the development of columnar structures. The **columnar growth (CG) mode** may eventually reduce the number of grain- or subgrain boundaries by a coarsening effect. However, the resulting mosaic structure is associated with crystal defects and may result in an inhomogeneous incorporation of dopants and inferior electrical or optical performance of devices fabricated from such films. The most extreme examples of columnar growth may be observed in electrodeposition at very high current densities (and therefore effective supersaturations). The term botryoidal, meaning looking like a bunch of grapes, is used to describe unstable columnar growth.

In recent years there has been increasing use of substrates with a deliberate misorientation with respect to the crystallographic plane. If the angle and direction of the misorientation are carefully selected, two-dimensional nucleation can be suppressed or at least reduced and the VW, SK, SI or CG modes can be suppressed. The resulting **step-flow (SF)** mode allows the preparation of relatively flat surfaces, but at the cost of high step densities. The interstep distance is similar to that in the VW, SK or SI modes and depends on the actual supersaturation. The surface in the SF mode can be regarded as a relatively rough surface which is sensitive to local variations, leading to undulating variations in thickness. Rejection of impurities is not very effective.

Step-bunching (SB) is observed when a high density of steps moves with relatively high speed over the surface. Fluctuations lead to the later-grown steps catching up with the earlier layers to move together as macrosteps. Macrostep formation is a very common feature of crystal growth and can be described by the Lighthill-Whitham (1955) traffic flow theory as discussed in Chapter 4. At low supersaturation, step bunching can be suppressed by the transition to faceting, as shown by Scheel (1980) and by Chernov and Scheel (1995).

Growth on kinked surfaces (KS) is applied in LPE of rare-earth garnets for magneto-optic applications onto (111) substrate surfaces.

Seven modes of epitaxial growth have been discussed in some detail by Scheel (1997), along with original references to these various growth modes.The additional growth mode on kinked surfaces (KS mode) was added in a later review of Scheel (2007). The in total eight growthmodes – FVM, VW, SK, CG, SI, SF, SB and KS are shown for three successive stages of growth in Fig. B.1.

From the viewpoint of crystal growth, the important question is how the mode of growth may be controlled. Especially it is desirable to establish conditions for FVM growth, since this results in epitaxial layers with the highest crystallographic quality. In film deposition by PVD or CVD, the effective supersaturation σ is high, and two-dimensional nucleation occurs with the critical radius of surface nuclei given by

$$r_s^* = \gamma_m V_M / a^2 RT \sigma \qquad \text{(B1)}$$

where γ_m is the energy per growth unit, V_M the molar volume and a the lattice constant. At medium and low supersaturation, the propagation of growth steps

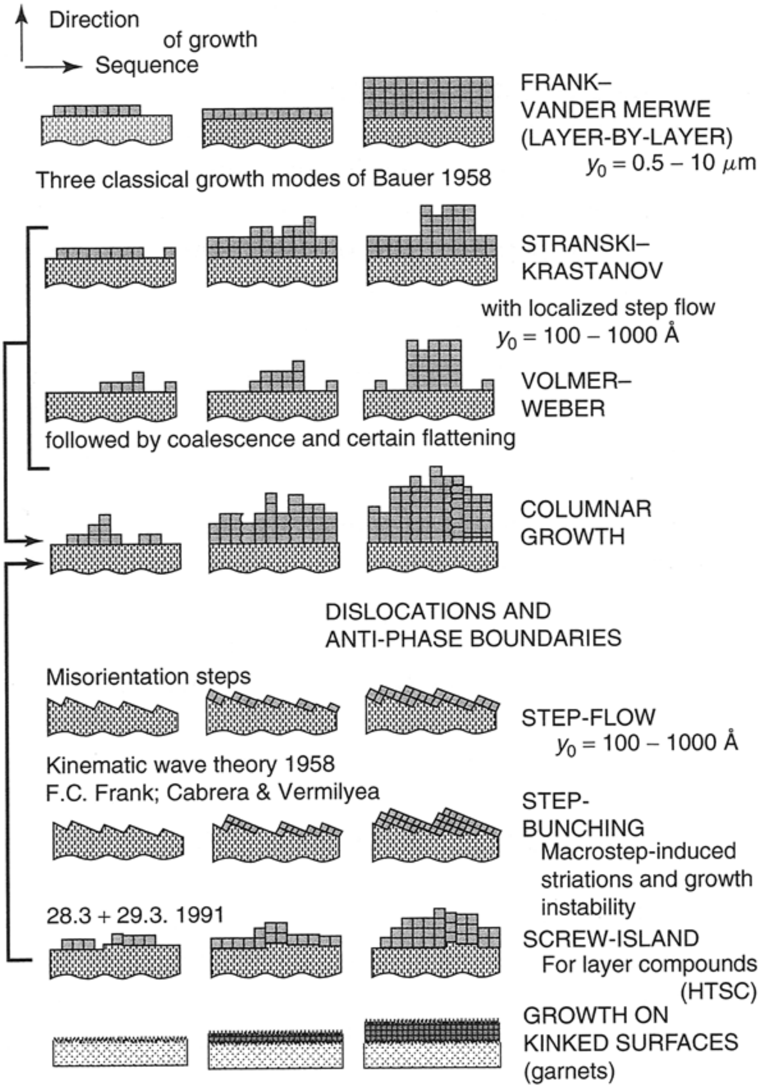

Fig. B.1.Eight modes of epitaxial growth, shown at three successive stages in each case (Scheel 1997, 2007).

may be observed. The distance between steps is equal to

$$y_o = 19\, r_s^* \,. \tag{B2}$$

In the presence of screw dislocations which lead to growth spirals, the BCF theory predicts an Archimedian spiral with step distance of $4\pi\, r_s^*$. As an example of interstep distance, Scheel (1980) reported a measurement of 6 µm for LPE-grown gallium arsenide. Interstep distances of only 50 nm are typical for MBE and MOCVD of this material.

The strategy to control the mode of epitaxial growth is shown in Fig. B.2, where the size of the critical surface nuclei and the interstep distance are plotted against the supersaturation. Typical supersaturation ranges for the various methods of epitaxial growth are also shown, together with the characteristic mode of growth. In MOCVD and MBE the supersaturation is relatively high, with the consequence that growth occurs by two-dimensional nucleation in the VW, SK or SI modes. The density of solid gallium arsenide is 5.3 g/cm^3, but its density in the vapor phase during MOCVD is typically 0.0065 g/cm^3, three orders of magnitude lower. The supersaturation, the driving force for deposition, is governed by this ratio. Since the majority of structural defects occur when growth islands coalesce, high structural perfection and excellent surface flatness are not possible when the supersaturation is high. In contrast, the concentration of the species to be deposited by LPE is typically around 10%, corresponding to the solubility in the liquid phase.

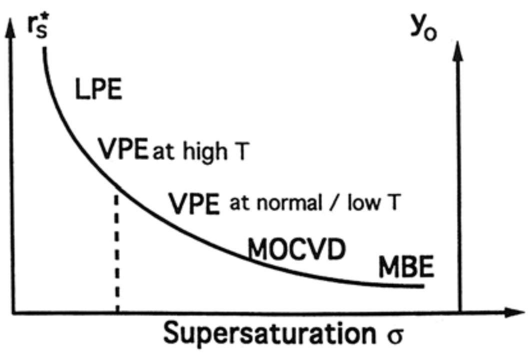

Fig. B.2. Influence of supersaturation on radius r_s^* of critical surface nuclei and on interstep distance y_0. Typical growth modes for the different methods of epitaxial growth are also shown.

By far the best structural perfection, and surfaces that approach atomic flatness, can be achieved in the FVM growth mode which requires very low supersaturation. This FVM mode can only be achieved by a near-equilibrium growth process such as LPE. The complexity of LPE using high-temperature solvents in a multi-parameter process is such that proper process control is often not achieved, so that films of high quality are not produced. This failure in much early LPE work to realize the full potential of this method has led to a tendency to associate LPE with poor structural perfection, as exemplified by the meniscus lines in LPE growth of gallium arsenide. However, when care is taken in substrate preparation, process atmosphere and growth conditions, quasi-atomically flat surfaces can be produced. An example of extremely flat surfaces produced by LPE was reported by Scheel, Binnig and Rohrer (1982). This was the first investigation of an epitaxial surface by the then original method of scanning tunneling microscopy, for which the two latter authors were awarded the Nobel physics prize.

Much of the above discussion has been concerned with homoepitaxial growth, and the role of misfit between the film and substrate has not been addressed. Frequently, as in the case of gallium nitride films, deposition is onto substrates with large mismatch in lattice constant and thermal expansion coefficient, and these factors clearly affect the quality of the film deposited. Misfit normally induces the VW mode, except for large interface energies between substrate and deposit which will cause the SK mode. Grabow and Gilmer (1988) have shown that the pure layer-by-layer (FVM) mode requires close to zero misfit. Experimentally it is found that epitaxial deposition can be achieved at the high supersaturations of VPE even at large misfit. In LPE, the necessary supersaturation for epitaxial growth increases with the misfit, so that step bunching or even 2D nucleation may be observed due to this high supersaturation. The high structural perfection possible with the FVM mode can therefore only be realized if the misfit is small. The relationship between supersaturation, misfit and growth modes is illustrated in Fig. B.3, which also shows the regimes of the major growth techniques.

Well-controlled LPE processing to produce extremely flat epitaxial surfaces is likely to become of great importance as the need for high structural perfection becomes more widely recognized. As an example of what can be achieved, red light-emitting diodes of great brilliance (15 Cd) and clear green LEDs were reported by Nishizawa and Suto (1994) and are manufactured by the Stanley Corp. in Tokyo. If the efficiency of LEDs could be further improved, and lifetime increased by the reduction in structural defects, we could envision a trend to replace the inefficient light sources such as traffic signals by solid state LEDs. Incandescent and fluorescent lamps could be replaced by UV-diodes based on GaN, combined with a phosphor, to form white LEDs for general illumination. This would result in major energy savings and contribute to alleviating the global warming problem. Numerous devices based on III-V compounds, also the most efficient infra-red detectors, are already fabricated on films deposited by LPE. Ultra-high speed electronic devices using the high-temperature superconductors require extremely well-defined, thin layers for functional structures based on electron tunneling. Quantum well and quantum dot structures could be fabricated in improved quality using LPE. Solar cells with efficiencies of 25-35% will be necessary at some

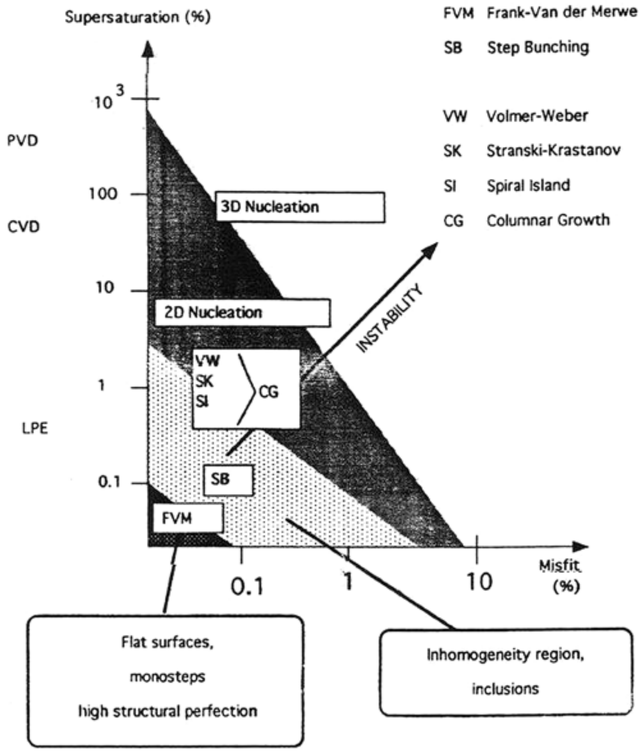

Fig. B.3. Occurrence of the seven epitaxial growth modes as a function of supersaturation and misfit. The high supersaturation of physical vapor deposition (PVD) and chemical vapor deposition (CVD) normally excludes the FVM mode except for rare cases like silicon where high growth temperatures and homoepitaxy are possible.

point in our history as non-renewable energy reserves become depleted. The technology base to fabricate such devices is known, but major cost savings will be necessary, by the use of LPE on a large scale to manufacture devices for mass production of high-efficiency photovoltaic panels. Silicon carbide is an emerging material for electronic devices capable of operation at high temperatures; LPE has the demonstrated capability to heal micropipe defects which are formed in SiC substrate wafers and have a detrimental effect on devices fabricated in epitaxial layers deposited from the vapor phase. These few examples will no doubt be followed by several others but serve to illustrate a need for intensive development so that this important technology of LPE can achieve its true potential. This requires the education of crystal/epitaxy technologists (Scheel 2003&2004).

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