PERFECT CRYSTALS: PROPOSED EDUCATION OF CRYSTAL TECHNOLOGISTS

Hans J. Scheel
General Protection Engineering (GPE) GmbH Switzerland
Swiss Office : Bromattenweg 2, 3805 Goldswil b. Interlaken, Switzerland
Greek Office (October to May) : Poulithra, 22300 Leonidion, Greece
E-mail: hans.scheel@bluewin.ch www.hans-scheel.ch

Summary
The perfection of crystals and of epitaxial layers (“epilayers”) is a main factor for the quality of physical investigations and for the performance of devices in all fields of applications. In the early phase of crystal growth in the 19th century and most of 20th century the crystal perfection depended on the intuition and experience of the crystal growers. These experts often kept their procedures and details of the growth process secret. Thus crystal growth was often regarded by physicists as cooking by recipes. With the formation of national and international crystal growth organizations from the 1960s/1970s and the corresponding conferences the exchange of experiences and the scientific approach to crystal growth started. However, there are typical 10 to 12 or more parameters which have an impact on the growth process and thus on crystal perfection. The involvement of the three aggregates vapor, liquid and solid and their phase transitions and interdependences on the one hand, and the most important growth parameters growth temperature, temperature gradient, supersaturation, hydrodynamics/aerodynamics establish an enormous complexity. Thus the theoretical understanding of real growth processes still is marginal. Some progress was achieved by computer simulation of industrial crystal production.
In the following a few empirical approaches to achieve large perfect crystals from (high-temperature) solutions will be discussed [1]. The first problem is to find a **solvent system** where the solute has sufficient solubility (preferred more than 5%), where the solvent is not incorporated in the crystal by different valency or ionic radii, and where the solubility curve allows precise control of supersaturation. **The control of nucleation for achieving large crystals** requires an extremely clean solution free from any solid particles, a container surface without epitaxial and topotaxial structures, a homogeneous solution achieved by forced convection (thereby considering the metastable Ostwald-Miers region), the precise control of temperature and temperature gradient, and providing a nucleation site by localized cooling or by a seed crystal.
Inclusions are a common problem in growth from solutions and can be prevented by reducing the diffusion boundary layer thickness by forced convection combined with calculated supersaturation control for the **maximum stable growth rate** [2] or in highly concentrated solutions by preventing **diffusional undercooling** of Ivantsov [3] by stabilizing temperature gradients respectively **constitutional supercooling** derived later by Tiller et al. [4].
Inhomogeneity has long been regarded as problem, the **striation problem**. These growth bands were related to convective instabilities so that large expensive efforts in microgravity in Skylab/Spacelab were undertaken to minimize natural convection. However, zero gravity cannot be achieved over extended periods, and without convection the stable growth rate becomes

excessive long so that large inclusion-free crystals cannot be grown in space. The author has developed smooth forced convection by acceleration and deceleration of crucible rotation, the Accelerated Crucible Rotation Technique ACRT [5]. This allows higher stable growth rates by reducing the diffusion boundary layer, nucleation control, and in combination with very precise temperature control by means of the PtRh6 versus PtRh30 thermopyle [6] and optimized programming of supersaturation the **first growth of striation-free solid-solution $KTa_{1-x}Nb_xO_3$ (KTN) crystals** together with Daniel Rytz [7]. The theory of striation-free growth and the derivation of the effective distribution coefficient for growth from solutions was developed with Bob Swendsen [8]. Dislocation-free $SrTiO_3$ crystals are achieved by inclusion-free growth from solutions and minimum contact with crucible surface [9].

Highest perfection with lowest dislocation density can also be achieved in epitaxy at very low supersaturation. Stringfellow showed in a diagram the large difference in supersaturation for GaAs for epitaxy from the vapor phase (~75 kcal/mole) and the very small driving force of <0.03kcal/mole for liquid phase epitaxy LPE [10]. Only by LPE, near thermodynamic equilibrium, the multiple surface nucleation and island formation by Volmer-Weber or Stranski-Krastanov growth mode can be prevented and **dislocation-free atomically flat surfaces** be obtained by the Frank-Van-der-Merwe growth mode as was shown for GaAs [11, 12], for high-temperature superconductor $YBa_2Cu_3O_{7-x}$ [13], and theoretically with A. Chernov [14]. The **control of 8 epitaxial growth modes** and their role in layers and multilayers was discussed in [15, 16].

Enhanced progress in crystal growth and thus in sciences and technologies, especially in energy technology, requires **education of crystal technologists** which will be briefly discussed and is described in a WHITE PAPER (17).

[1] D. Elwell, H.J. Scheel: Crystal Growth from High-Temperature Solutions, Academic Press (1975), online edition with Ch. 11 and two appendices in www.hans-scheel.ch
[2] H.J. Scheel, D. Elwell, J. Crystal Growth **12**, 153-161 (1972)
[3] G.P. Ivantsov, Dokl.Akad.NAUK SSSR **81,** 179 (1951), **83**,573 (1952)
[4] W.A. Tiller, K. A. Jackson, Rutter, B. Chalmers, Acta Met. **1**,428 (1953)
[5] H.J. Scheel, J. Crystal Growth **13/14**, 560-565 (1972)
[6] H.J. Scheel, C.H. West, J.Phys.E: Scientific Instruments **6,** 1178 (1973)
[7] D. Rytz, H. J. Scheel, J. Crystal Growth **59**, 468-484 (1982)
[8] R.H. Swendsen, H.J. Scheel, J. Crystal Growth **233**, 609-617 (2001)
[9] H.J. Scheel, J.G. Bednorz, P. Dill, Ferroelectrics **13**, 507-509 (1976)
[10] G.B. Stringfellow, J. Crystal Growth **115,** 1(1991)
[11] H.J. Scheel, Appl. Phys. Lett. **37,** 70-73 (1980)
[12] H.J. Scheel, G. Binnig, H. Rohrer, J. Crystal Growth **60**, 199-212(1982)
[13] H.J. Scheel, C. Klemenz, F.-K. Reinhart, H.P. Lang, H.-J. Güntherodt, Appl. Phys. Lett. **65**, 901-903 (1994)
[14] A.A. Chernov, H.J. Scheel, J. Crystal Growth **149**, 187-195 (1995)
[15] H.J. Scheel, Proceedings Internat. Symposium on Laser & Nonlinear Optical Crystals, editor T. Sasaki, Data Storage Institute, Singapore, 10-18 (1997)
[16] H.J. Scheel, Ch. 1 in “Liquid Phase Epitaxy”, eds. P. Capper, M. Mauk, Wiley (2007)
[17] F.J. Bruni, H.J. Scheel: White Paper in www.hans-scheel.ch