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# Growth of Extremely Flat Semiconductor and Superconductor Layers by Liquid-Phase Epitaxy(液相エピタキシャル法による極めて平坦な半導体および超伝導体層の成長)

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# 論文内容要旨

Flat surfaces and quasi atomically sharp interfaces in superlattice structures are becoming of increasing interest for various fields of science and branches of technologies.

In this work the parameters of epitaxial deposition by physical vapor deposition PVD, chemical vapor deposition CVD, and liquid-phase epitaxy LPE are analyzed and compared. The large differences between growth from vapor and from liquid with respect to concentration and to supersaturation explain the low growth rates and large step densities in vapor deposition, and the relatively high growth rates and very low step densities in liquid-phase epitaxy. Epitaxial growth by one of the three classical growth modes (Frank-Van der Merwe, Stranski-Krastanov, Volmer-Weber) or by the new spiral-island growth mode is not only determined by supersaturation, but depends also strongly on misfit and substrate misorientation. Questions still to be answered are whether the spiral-island mode occurs only with layer structures, and how it relates to misfit. From this follows that by PVD and CVD quite flat surfaces with high step densities ( $5 \times 10^5$/cm) can be achieved on critically misoriented substrates, and these surfaces are very active in catalysis, corrosion, crystal growth, and in the case of YBCO in oxygen loss and uptake.

On LPE surfaces grown on-facet the interstep distances can be very large, typically a few μm, theoretically without limit, so that step densities are about 2000/cm. Such surface can be quasi atomically flat, they are inactive, and they are desirable for specific surface studies like surface enhanced Raman spectroscopy, angle-resolved photoemission spectroscopy etc. The greatest importance LPE-grown facets may obtain in specific technologies where surface flatness is of crucial importance. One example is high-temperature superconductivity HTSC where planar surfaces are required for the depelopment of a reliable planar tunnel-device technology. Another advantage of such extremely flat surfaces with mono-or double steps is the single growth mode which results in an extraordinary homogeneity of the layers, a homogeneity which perhaps can not be achieved by any other growth technique. Therefore LPE-grown layers and surfaces may become of value for future technological developments in micro-and optoelectronics, optical communication technology, and high-$T_c$ superconductivity.

The achievement of quasi atomically flat surfaces is demonstrated with two different classes of materials of technological interest : the semiconductor GaAs and the high-$T_c$ superconductor YBCO.

In the first case a sliding-free technology MultiLPE was developed which allows the unconstrained growth of GaAs multilayers and superlattices with extremely flat interfaces and surfaces. The double-screw device is slowly rotated so that separate solutions wash over the substrates and return to the starting position by the internal screw with reverse sense, see Fig. 1.

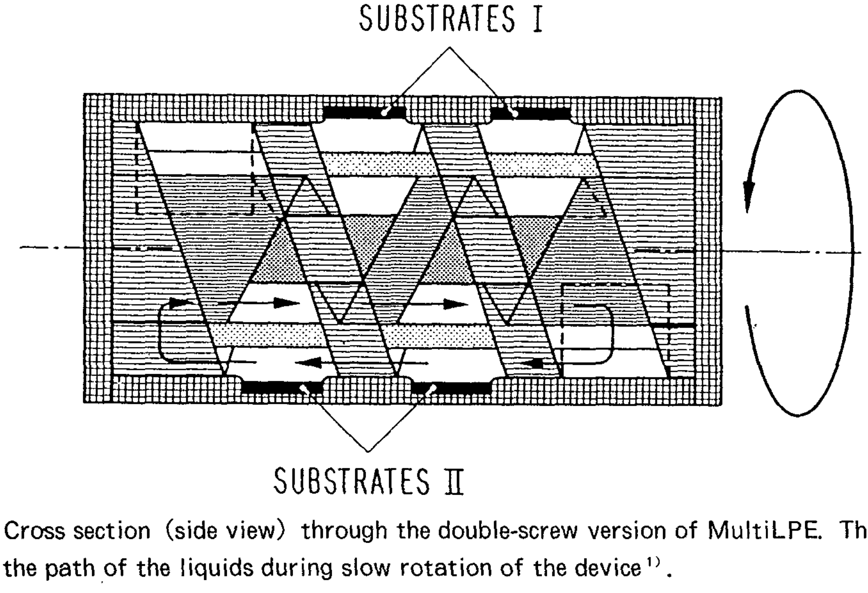

Fig. 1. Cross section (side view) through the double-screw version of MultiLPE. The arrows indicate the path of the liquids during slow rotation of the device[1].

The initial wetting problem, causing a remaining liquid film on the substratre surface, was due to contamination of the Ga solutions. A glovebox-furnace system and a He-H$_2$ atomosphere with recycling and purification were developed by which $<0.03$ ppm O$_2$ and $<0.05$ppm H$_2$O were achieved. This allowed to solve the wetting problem. During multilayer growth the transition from misoriented substrates to faceting was reproducibly observed. This is shown in Fig. 2.

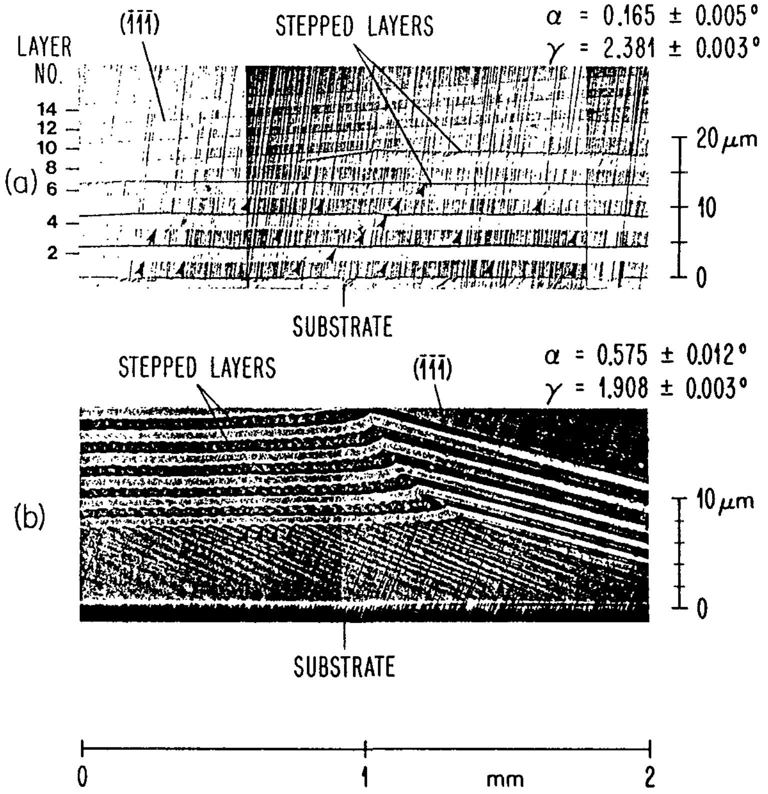

Fig. 2. Two examples of the transition to faceting from two substrates of misorientation 0.165° and 0.575°, respectively. The 12- to 14-layer structures of alternating p- and n-GaAs are anglelapped ($\gamma \approx 2°$) and etched. In example a) the facet starts with layer 8 and is complete with layer 12. Example b) is only partially facetted due to large misorientation angle[2].

Such a GaAs facet was the first epitaxial surface investigated in the novel scanning tunneling microscope by Binnig and Rohrer. The distance between steps was 6 $\mu$m (Nomarski differential interference contrast microscopy), and the step height by STM 6.5 Å. The Nomarski picture is shown in Fig. 3, the STM results in Fig. 4.

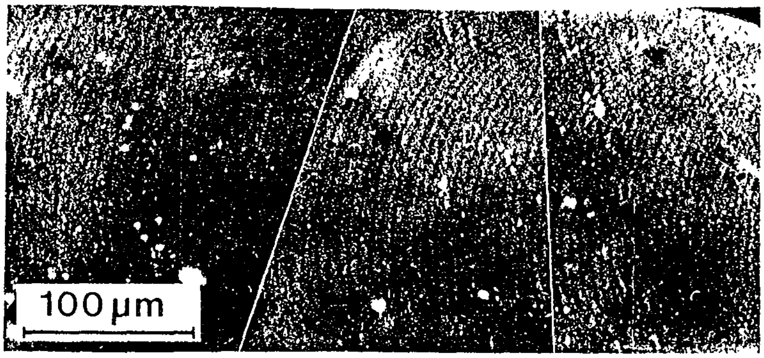

Fig. 3. Composite interference contrast (Nomarski) micrograph of the surface of a facet. The rounded steps of less than 10 Å height and mean distance of 6 μm originate from the edge of the facet2).

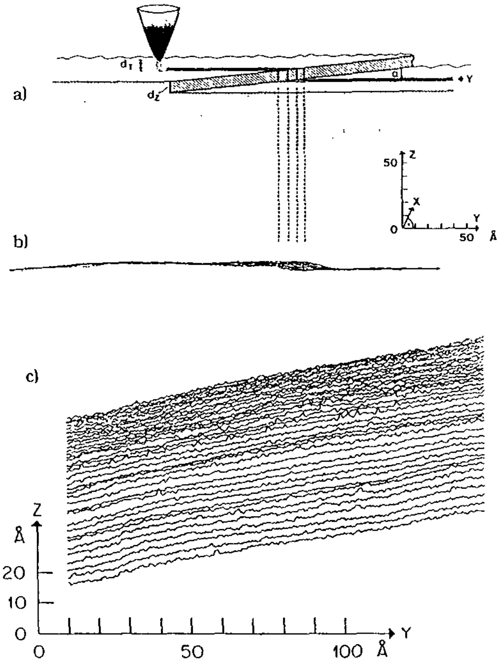

Fig. 4. STM investigations of the facet shown in Fig. 3. a) Schematic sample arrangement in front of the tunneling tip with the coordinates and the lateral and height scales. The step of height $d_z$ makes the angle $\alpha$ with the scan direction Y. b) Multiple STM scan showing an atomically flat surface with a step about 6.5 Å high on the GaAs (111) facet. c) STM contour lines of the facet which is scanned in Y-direction at $\Delta X$ displacements of 4.5 Å. The surface is flat within about 3 Å over an area of 170x130 Å$^2$ 3).

The principle of MultiLPE is based on the relative motion between two (or more) growth liquids and any number of substrates by using gravitation in combination with rotation, tilting or any other motion of the container, thereby without any sliding parts. Epitaxial layers are deposited during the contact time of the substrate with the supersaturated solution. Many topologies can be thought of, which allow by this principle the sliding-free fabrication of multilayer structures, from laboratory scale to mass production ($km^2$ per month). Layer thickness can be varied from monolayers to mm, and total superlattice thickness can exceed 1 cm. With a specific topology also the sequence control of layers and thickness variations can be achieved, also replenishing, doping and exchange of solutions. Obviously is such a technique not limited to GaAs, it is applicable to all classes of materials which can be deposited from liquids (solutions), and even to material combinations when the crucible／atmosphere compatibility is not a problem. Thus MultiLPE opens a new dimension in materials science and solid-state and device physics.

The high-Tc superconductor YBCO (and NdBCO) is the second example where extremely flat surfaces have been achieved for the first time. Initially the prerequisites for LPE of YBCO had to be established : a homogeneous solution and nucleation control, the primary crystallization field and the solubility curve, after crucible corrosion studies the development of yttria crucibles (which are now commercially available), apparatue and process. The substrate problem is yet only partially resolved, and also the oxidation／phase transformation／cracking problem has still to be solved. Under these conditions very promising results were obtained : layer-by-layer growth over mm dimensions, typical interstep distances between 0.5 and 3 $\mu$m (in contrast to PVD- and CVD-grown YBCO with 0.01 to 0.05 $\mu$m step distances and spiral islands) and step heights between monosteps and 70 Å steps. Fig. 5 shows a LPE-grown surface with mono-and double steps by AFM.

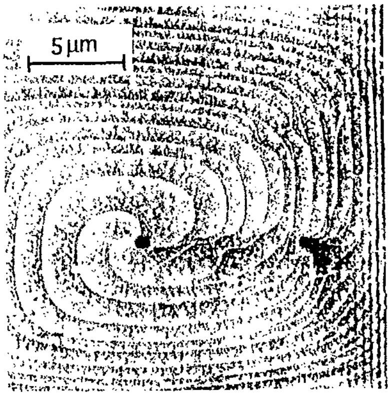

Fig. 5. LPE-grown YBCO surface seen by atomic-force microscopy[4]. A single-core spiral with a distant disturbance consists of double steps which split in the lower right corner into monosteps.

Further development should lead to interstep distances of 10 μm as required for planar HTSC tunnel-device technology. Fig. 6 shows a comparison of PVD- and LPE-grown surfaces and the surface required for HTSC tunnel technology with step distances> 10 μm.

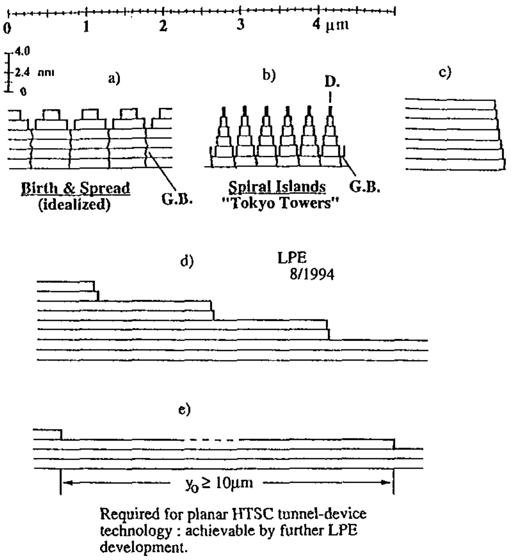

Fig. 6. Schematic cross sections of vapor-grown structures with idealized birth-and-spread mode (a), of a PVD-or CVD-grown layer (b), of a layer with the critical misorientation to suppress islands (c), for a LPE-grown structure (d), and for a surface required for HTSC tunnel device technology. The horizontal and vertical scales are the same for all figures and are given at the top⁵⁾.

It can be concluded that by LPE quasi atomically flat surfaces can be achieved, also multilayers/superlattices in laboratory scale up to mass production. However, to develop LPE for a new material can be quite demanding. To establish the prerequisites and to optimize the many growth parameters may take months or years.

Physical vapor deposition (MBE, sputtering etc.) is much more flexible and well-suited for the fast developmant of novel multilayer and device structures : PVD are indispensable in R&D on layered structures, even at the cost of inherent high step densities. CVD lies between PVD and LPE, more on the PVD side as a research tool with no serious scaling-up problems for mass production.

Finally, it should be remarked that the low-threshold semiconductor Raman laser demodulator for optical signals in the terahertz frequency range developed at the Tohoku University and at the Semiconductor Research Institute Sendai are based on LPE under controlled vapor pressure using the temperature-difference method (K. Suto, T. Kimura, J. Nishizawa, IEE Proc. -J. **138** (1991) 396, **139** (1992) 407 and J. Electrochem. Soc. **140** (1993) 1805). This is one example of highest performance devices developed from LPE-grown layers. PVD, CVD, and LPE have weaknesses and strengths, they complement each other, so that all three approaches are required for advances in electronic and optoelectronic technologies.

1) H. J. Scheel, J. Crystal Growth **42** (1977) 301.

2) H. J. Scheel, Appl. Phys. Lett. **37** (1980) 70.

3) H. J. Scheel, G. Binnig and H. Rohrer, J. Crystal Growth **60** (1982) 199.

4) H. J. Scheel, C. Klemenz, F. −K. Reinhart, H. P. Lang and H. -J. Güntherodt, Appl. Phys. Lett. **65** (1994) 901.

5) H. J. Scheel, in Advances in Superconductivity VI (Proceedings of the 6 th Internat. Sympos. on Superconductivity ISS'93, Hiroshima Oct. 26-29, 1993) editors T. Fujita and Y. Shiohara, Springer, Tokyo 1994, 29.

# 審査結果の要旨

超格子，多重量子井戸デバイス，あるいは超伝導ジョセフソン素子などの微小な電子デバイスは，原子的に微細な領域で機能しなければならない。このためには原子的に平坦なエピタキシャル成長が必要となる。本研究は，液相成長法によって，化合物半導体GaAs多重層，および高温超伝導体$YBa_2Cu_3O_{7-x}$（YBCO）層の極めて平坦なエピタキシャル成長をおこなった結果を纏めたものであり，全編4章よりなる。

第1章では本研究の背景を述べた後，エピタキシャル成長における，表面の原子ステップの間隔が成長法によってどのように違うかを論じている，原子レベルでの制御性が高いと言われている分子線エピタキシ法のような物理的気相堆積法（PVD），有機金属堆積法のような化学的気相堆積法（CVD）と，液相成長法（LPE）を，過飽和度を尺度にして比較している。LPEでは，過飽和度が小さいため二次元成長核の臨界半径が大きい。その結果，単原子ステップ間隔はGaAs層およびYBCO層のいずれにおいても，LPE法では，PVD，CVD法での100倍程度にも及ぶとしている。

第2章では，GaAs多重層の液相成長について述べている。従来，各種のデバイスに必要な多重エピタキシャル層を液相成長法によって得るには，スライダーを使用する方法が一般的であったが，層数に限度があり超格子のような多数の層を成長することは困難であった。著者は，2重スクリュー構造を有する新規な成長装置を考案し，15層におよび，かつ，極めて平坦な多重エピタキシャル層の成長を可能にした。走査トンネル顕微鏡（STM）を考案したG. Binnig，H. Rohrerと共同ではじめて液相成長層の表面のSTM観察を行い，またノマルスキー干渉顕微鏡も用いて，高さ6.5Aの原子ステップが6 μm程度の間隔で存在することを示した。これはPVD，CVD法で得られるGaAs表面の原子ステップ間隔の100倍程度であり，LPE法によって，極めて平坦な，多層エピタキシャル成長が可能なことを示したことになる。

第3章ではYBCO層の液相エピタキシャル成長について述べている。まず，腐食による汚染を生じない$Y_2O_3$坩堝を開発するなど，エピタキシャル成長の要素技術を開発した。基板単結晶として格子不整合度が1％以下である$NdGaO_3$を選び，基板単結晶を溶液中に浸し回転させる方法で，世界で初めて液相法による高温超伝導体のエピタキシャル成長に成功した。更に，エピタキシャル成長層の表面に，2から5原子層の高さのステップが1から6 μm程度の間隔で存在することを示した。ステップ間隔はGaAsの場合と同様に，PVD，CVD法の100倍程度であり，液相成長法によって極めて平坦な高温超伝導体層が得られることを示した。

第4章は総括である。

以上要するに本論文は，液相成長法によって，化合物半導体GaAs多重層および高温超伝導体$YBa_2Cu_3O_{7-x}$層の，原子的尺度で極めて平坦なエピタキシャル成長が可能であることを示したもので，材料工学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。