

A NEW TECHNIQUE FOR MULTILAYER LPE

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A novel technique is presented which allows LPE deposition of a large number of layers without the disadvantages arising from sliding container parts. Solutions of different compositions or containing different dopants are arranged in separate chambers. By rotation of the whole device the solutions move from one chamber to the next one without intermixing, and by controlled cooling, epitaxial layers are deposited onto the substrates fixed at the chamber walls. The sequence of the layers is determined by the sense and the angles of rotation, and the thickness of each layer is determined, among many other factors, by the cooling rate and dipping time. Up to 15 layers of III–V compounds have so far been produced in a double-screw device, with thicknesses between 0.1 to 10 μm and a thickness reproducibility of about 10%. In addition, the fabrication of LED's, III–V lasers, and solar cells, and possibly superlattice devices by the MultiLPE technique can be considered.

1. Introduction

Successive deposition of semiconductor layers of varying composition and type of dopant by liquid phase epitaxy has resulted in highly efficient light-emitting diodes [1], III–V solar cells [2], and semiconductor lasers [3] of long lifetime [4]. The LPE preparation of superlattice structures has been attempted [5], however, the results did not fulfill the stringent requirements of very thin layer thicknesses, e.g. about 100 Å, for superlattice devices [6].

The commonly applied sliding systems of graphite [7–10], silica glass or alumina [11] impose strict geometrical conditions: a too wide gap between substrates and sliders leads to mixing of successive solutions, a too narrow gap causes scratching of the grown layers. In any case the number and thickness of layers are restricted. Other disadvantages are scratched-off carbon particles and the frequently observed meniscus lines [12] which, among other factors, limit the efficiency of III–V lasers [13,14]. Advantages of modern sliding systems are the thin solution layers [9,15–17] (allowing preparation of flat thin layers without constitutional supercooling [18]), and the mechanical removal of oxidized-melt surface layers [19] so that virgin solution surfaces contact the substrates.

A technique has been developed [20–22] which overcomes most of the above problems since no

sliding parts are required. There are practically no constraints as to number and thickness of deposited layers. The principle and the problems of this *Multi-LPE* technique will be outlined, and apparatus design and first experimental results will be discussed briefly.

2. Principle of MultiLPE

High-mobility low-carrier concentration GaAs has been prepared by Vilms and Garrett [23] from a Ga solution contained in a horizontal graphite tube. By slow rotation, the substrates fixed to the container walls dip into the supersaturated solution, and after growth are freed from the solution by further rotation by about 180°. Although some restricted change of dopants would be possible via the gas phase, the preparation of multilayer devices does not seem feasible in this configuration.

In our MultiLPE [20–22] two or more solutions are contained in separate chambers and are separately moved from one chamber to the next by rotation of the device. Thus the different solutions successively contact the substrates which are fixed in the chambers or channels. The number and volumes of the solutions, or the number and size of the substrates determine the size of the multi-chamber device.

An example of the *double-screw version* of the

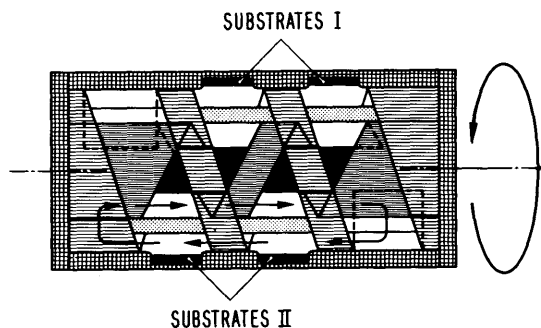


Fig. 1. Cross-section (side view) through the double-screw version of the MultiLPE technique. Inside the cylindrical tube the outer and the central screws with reversed sense are shown. The arrows indicate the path of the liquids during slow rotation of the device. Substrates I are used for saturating the solutions; on substrates II epitaxial layers are deposited from successive solutions.

MultiLPE technique [20,21] shown in fig. 1 (see also fig. 3), allows growth from two to five different solutions. These are contained in a horizontal tube and separated from one another by the walls of the graphite screws of which the outer one is tightly fixed in the tube, and the central screw of a reversed sense is fitted into the hollow shaft of the outer screw. Both screws are interconnected at both ends by channels. Mechanical tight fitting of the graphite parts is sufficient to prevent leakage (and thus mixing of successive solutions) since the high surface tension of gallium (of the order of 600–700 dyne/cm) and its large wetting angle on graphite prevents capillary flow between the contacting graphite parts.

By slow rotation of the whole device about its horizontal axis the different non-wetting solutions in the outer screw chambers are moved horizontally (see the arrows in fig. 1) until they reach the channel. By continuing rotation the solutions are successively forced into the central screw where they flow back by the reverse screw action to the channel at the other end, and then back into the outer screw for a new cycle. Thus by continuous rotation, all solutions circulate separately through the graphite device and once during their cycle pass all substrates which are fixed inside the device. The solutions remain completely separated provided they do not wet the container walls and are completely removed from the substrates after each growth period.

Another condition for keeping the solutions separated is a sufficiently low rotation rate. The acceleration of the liquid due to centrifugal forces must be significantly smaller than the earth's gravitation: $\omega^2 r \ll 981 \text{ cm} \cdot \text{sec}^{-2}$, where ω is the angular velocity in $\text{rad} \cdot \text{s}^{-1}$, and r the container radius in cm. If ω exceeds a critical value, which in addition is influenced by the degree of wetting and the viscosity, then a co-rotation of the liquid occurs, and at very high ω values the liquid is homogeneously distributed along the periphery of the container due to dominating centrifugal forces.

There is a certain resemblance of our double-screw version to the Archimedian screw which rotates inside an inclined channel or tube and which has been applied for more than 2000 years for uphill transport of water. However, our screws are fixed to the tube and merely serve for horizontal transfer of the liquids by combined rotation of screw and tube.

The double-screw version of the MultiLPE is one tested example of a variety of possible topologies [20,22], discussion of which would require too much space. It is merely indicated here that the version of an inclined tube with separation walls [22] might be preferable for certain applications, especially if a complex or nonperiodic sequence of layers are to be deposited. In most MultiLPE topologies the liquids are "rolling" during the rotation of the tube as indicated by the arrows in fig. 2a for the case of partial filling where the liquid has an unbounded upper surface. Tentative lines of identical flow velocity inside the rolling liquid are indicated. The dynamic wetting angle θ_A of the advancing liquid is expected to be slightly larger than the wetting angle θ_R of the receding liquid (as shown in fig. 2) due to friction [24]. At a higher filling degree, the liquid contacts the upper surface of the screw chamber. This causes a modification of the flow to a "double-roll" as indicated in fig. 2b.

Epitaxial growth of layers occurs during the time when the substrate is inserted into the supersaturated solution. Supersaturation may be achieved by programmed cooling or by step cooling, and in modified versions other ways of obtaining supersaturation (see ch. 7.1.2 and ch. 8 of ref. [25]) may be applied. The insertion time varies between seconds and hours for layer thicknesses of less than 1000 Å and more than 10 μm, respectively. For a given system the cooling

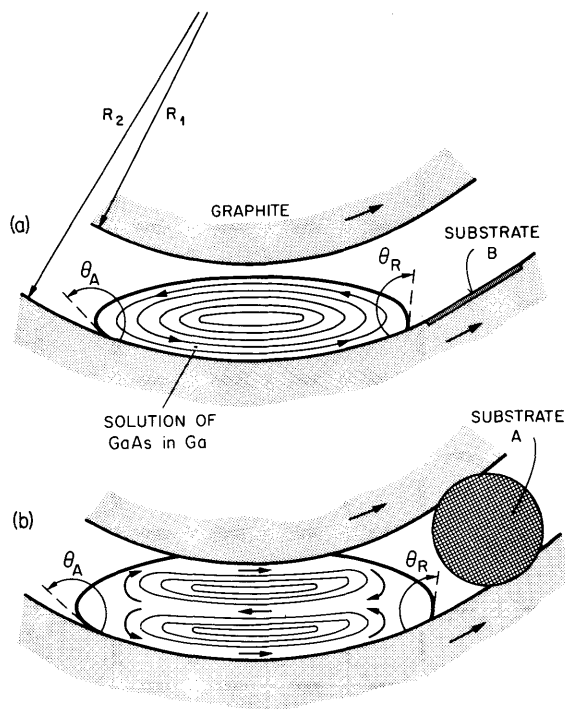


Fig. 2. Detail of the double-screw device indicating the "rolling" solutions (and two different substrate positions): (a) for a small liquid volume with a free surface, and (b) for a higher degree of filling resulting in a bound upper liquid surface.

rates are mainly determined by the maximum stable growth rate and by the ratio of substrate area and volume of solution, and typically lie between 1 and 10°C/h (they can be much higher when small or thin solution volumes or stabilizing temperature gradients at the interface are applied).

In accordance with Vilms and Garrett [23] the substrate positions A ("peripheral") and B ("vertical") shown in fig. 2 behave differently with respect to drainage of the gallium solution. The tendency for a thin solution to remain is larger on the peripheral substrate. This remaining liquid film causes aftergrowth during the cooling at the end of the experiment. On the other hand, remaining liquid films prevent the formation of "meniscus lines" [12,14] since the substrates are not dry (and thus do not have to be wetted) upon successive immersions. A disadvantage is the mixing of the remaining liquid layer with the next solution which thus limits the total number of layers that can be deposited. This disadvantage would

not allow the preparation of superlattices, but the fabrication of three to six layer devices like lasers, LED's and solar cells is not hindered, especially when intermediate cleaning solutions are used.

In addition to the usual purity and misfit problems of liquid phase epitaxy, in the MultiLPE technique there are the special problems of surface contamination and wetting. Oxide layers on the solution surface would prevent homogeneous wetting and growth of layers onto the substrates, and also substrate contamination has to be carefully prevented. The wetting problem will be discussed in the next section.

3. Wetting on containers and substrates

MultiLPE would not work for systems where the container is wetted by the solution, i.e., where the wetting or contact angle is smaller than 90° . Not only is wetting connected with the degree of corrosion, but also the adhering films of the different solutions would lead to mixing of subsequent solutions and thus drastically limit the applicability of MultiLPE. Absolutely tight mechanical designs would be required to prevent drainage of the wetting solutions by capillary forces which is not a problem when the solutions do not wet and have a high surface tension. Thus a suitable container material has to be chosen for the solution system desired, or a solvent which does not wet the containers used. In the case of metals and semiconductors growing from low-melting metallic solutions graphite, vitreous carbon, boron nitride and similar materials are suitable. Platinum-gold alloys or pure gold present themselves for the growth of oxides from borate solutions. Further data and references on container materials for a variety of high-temperature melts and solutions are given in ch. 7.2.3 of ref. [25].

Wetting data for several systems of interest are given in table 1. It should be remembered that measured wetting angles not only depend on the content of surface-active impurities and on surface contamination (oxide layers!), but also on the macroscopic roughness of the solid surface. According to the relation of Wenzel [30] $R = \cos \theta' / \cos \theta$ (where R is the roughness factor defined as the ratio of actual area of the surface to the apparent or flat area) the contact angle θ' increases with surface roughness for non-

Table 1
Wetting data for liquid gallium and aluminium

Solid	Liquid	Temp. range (°C)	Wetting angle (deg)	Ref.
Graphite	Ga	750/1000	130/120 (in H ₂) ^{a)}	[26]
Graphite	Al	700/1000	150/<90 ^{b)}	[27]
Silica glass	Ga	<950	No wetting ^{a)}	[11]
Silica glass, rough	Ga	750/1000	110/100 (in H ₂)	[26]
Silica glass, smooth	Ga	750/1000	125/100 (in H ₂)	[26]
Silica glass	Al	> melting point	Reaction	
GaAs-A (111)	Ga	35–331	113 ± 1 ^{c)}	[28]
GaAs-B (111)	Ga	46–479	143 ± 1 ^{c)}	[28]
GaP	Ga	750/1000	110/60	[26]

a) No wetting is observed according to our experience and wetting experiments.

b) Above 800°C, Al₄C₃ is formed at a significant rate if the Al surface is free from oxide [27].

c) Wetting of GaAs by Ga is affected by degree of misorientation and by surface roughness, but not affected by the atmosphere or by the type and concentration of dopants [29].

wetting liquids and decreases with wetting liquids. In addition, the wetting angles determined for thermodynamic equilibrium will be altered due to the non-equilibrium conditions during crystal growth and due to the motion of the liquids.

4. Growth experiments and results

The double-screw graphite device machined from high-purity graphite (Types EK 506 and EK 516 of

Ringsdorff/Germany) is shown in fig. 3. All graphite parts are heated in vacuum for 10 h (5×10^{-3} Torr, slow He inlet) at $1400 \pm 30^\circ\text{C}$ before use. The components of the two solutions for growth of p- and n-GaAs (5 g Ga, 335 mg GaAs, and 20 mg Ge or Sn, respectively) are filled into two separate chambers of the outer screw in a dry nitrogen atmosphere. The saturation and growth substrates (4.9 mm diameter, 4.5 mm free surface) are introduced and the cylindrical lid fitted to close the assembled graphite device. The latter is then horizontally fixed into a silica glass tube. This tube can be rotated and oscillated at adjustable speeds by a step motor and function generator. A PtRh6 versus PtRh30 thermocouple inside the graphite device indicates the temperature. The horizontal three-zone diffusion furnace (Kulicke and Soffa) is controlled by thermocouples near the heating elements and three Honeywell PI controllers, and programmed by an electronic ramp generator of Eurotherm. The precision is $\pm 0.1^\circ\text{C}$. During the experiments the silica glass tube is flushed with 250 l/h of palladium-diffused hydrogen.

The graphite device is heated to $830\text{--}860^\circ\text{C}$ and the solutions oscillated $\pm 25^\circ$ around a neutral position for 10–30 min. Then the temperature is lowered to the nominal saturation temperature of 820°C and the device turned in order to bring the solutions and the saturation GaAs (111) substrates I in B-position into contact (see fig. 1). These are oscillated in the

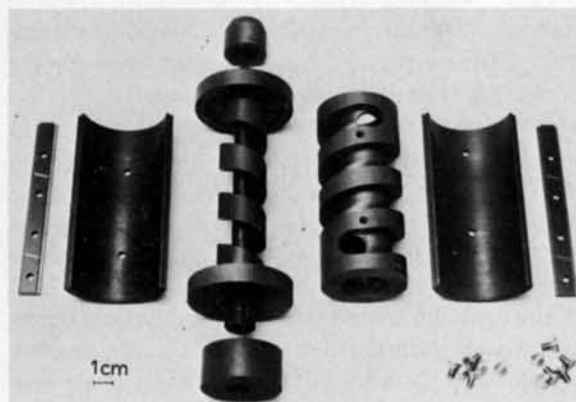


Fig. 3. Partially demounted graphite screws and other parts of the double-screw MultiLPE device. The small fitting screws are made from molybdenum. The substrates in A position are held by slits in the walls of the outer screw chambers.

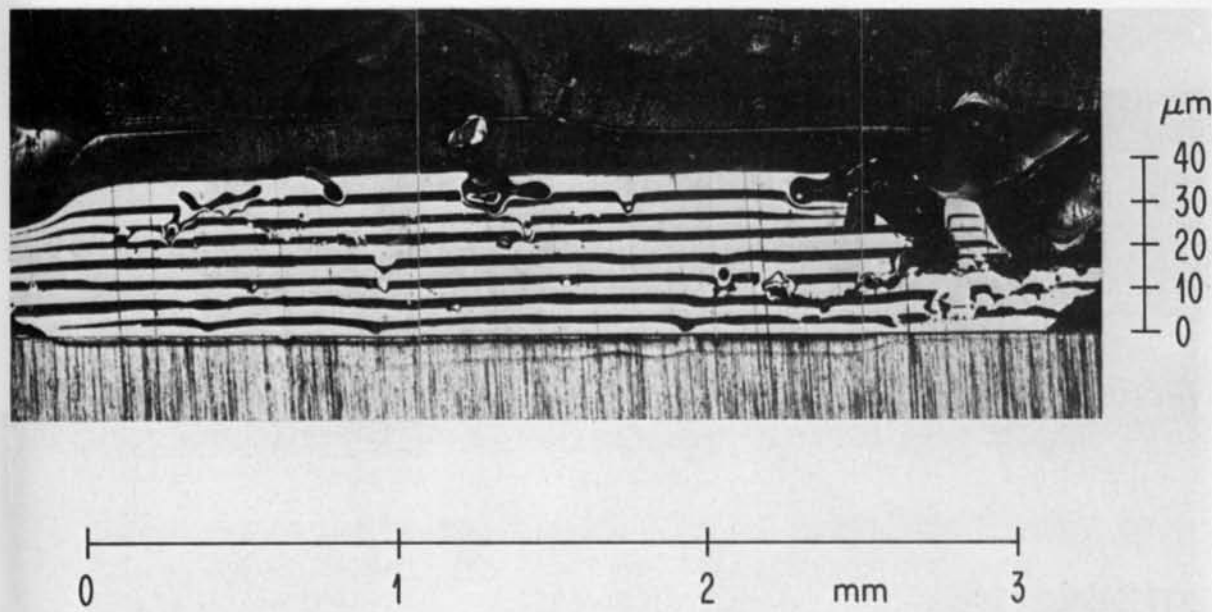


Fig. 4. Mounted Nomarski interference-contrast microphotographs of the angle-lapped 15-layer structure of alternating p- and n-GaAs layers. The average layer thickness is about 2 μm . Macroscopic defects due to solvent inclusions are clearly seen.

solutions, and the temperature is lowered to 818°C at a rate of 10°C/h. By further rotation of the graphite device the solutions are brought into contact with the GaAs (111) substrates II for ten minutes, and supersaturation is continuously achieved by programmed cooling (10°C/h) and the substrates being oscillated in the solutions. Every ten minutes the solutions in contact with the substrates are exchanged by appropriate rotation of the device until at the end of the experiment 15 layers of alternating p- and n-GaAs have been deposited.

The result of the experiment is shown in fig. 4. By angular lapping using diamond pastes of 3 and 1 μm followed by etching with diluted nitric acid (29 ml HNO_3 , 71 ml H_2O) in light [31] the 15-layer structure could be made visible. Inclusions (caused by constitutional supercooling) are clearly seen. Fig. 5 shows a SEM photograph of such an inclusion, and by X-ray fluorescence analysis pure gallium was detected in the unetched corners of the inclusion. Neglecting the initial transient of the growth rate, average values of 30 to 40 $\text{\AA} \cdot \text{s}^{-1}$ are found as the maximum stable growth rate [32] for various experiments where no stabilizing temperature gradients [33] and where

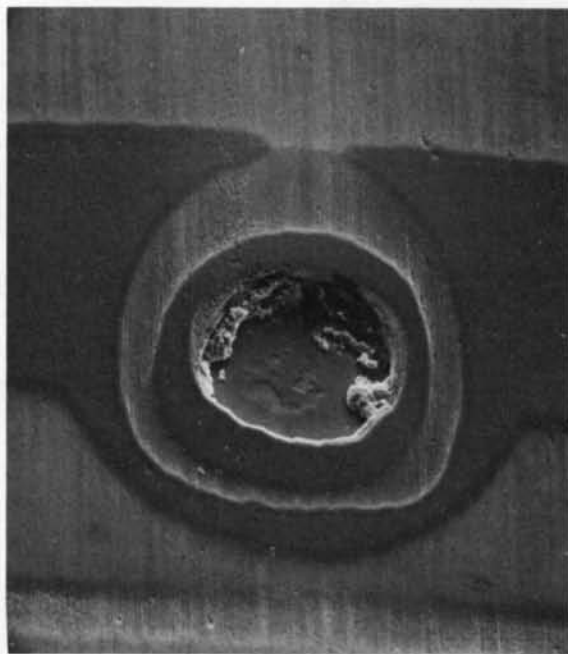


Fig. 5. Scanning electron micrograph of a macrodefect in the p-n-GaAs multilayer structure. On preparing the sample most of the Ga inclusion was etched, thus only in the corners are strongly electron-emitting (white) gallium traces found by X-ray fluorescence analysis.

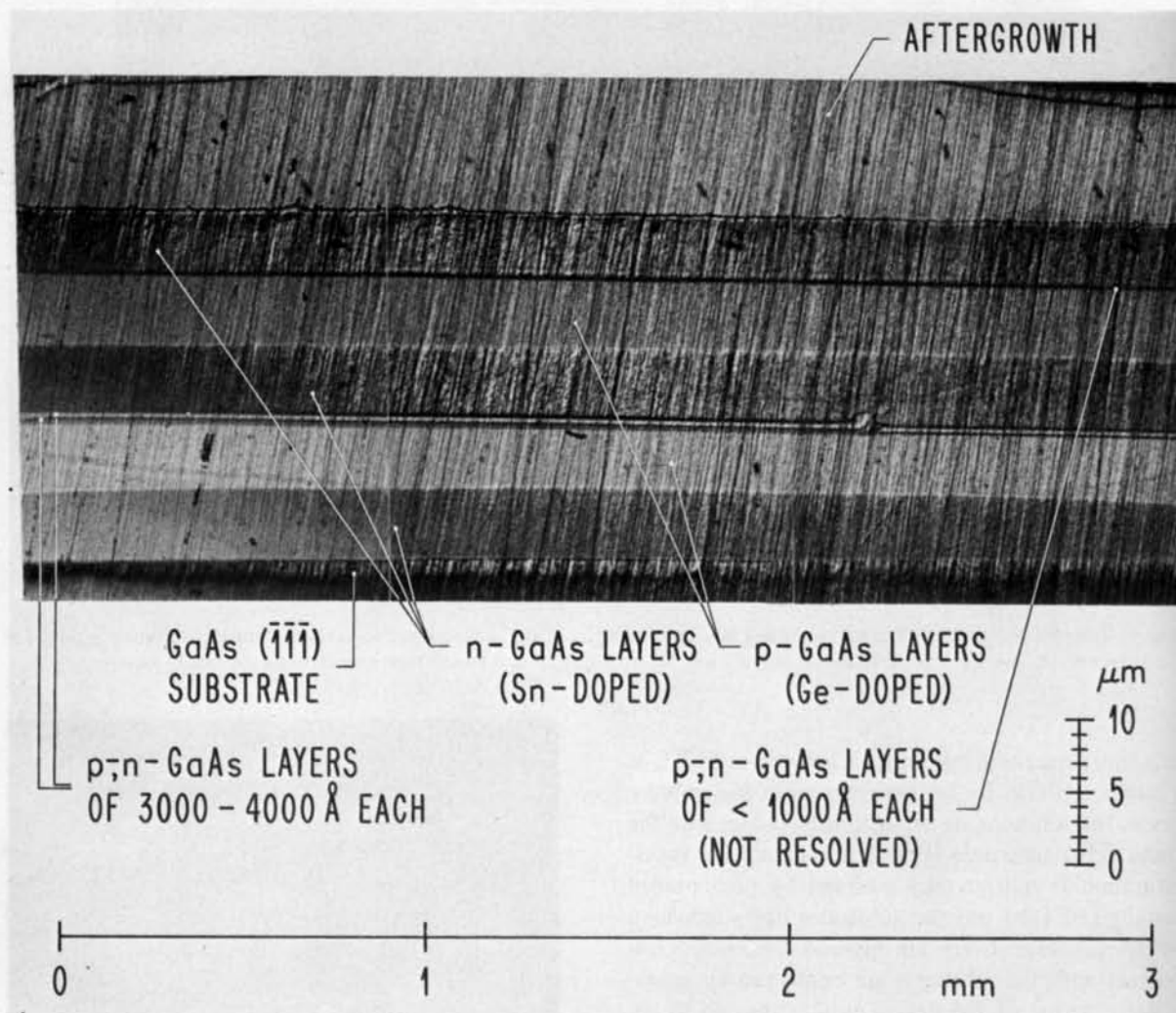


Fig. 6. Mounted Nomarski microphotograph of a MultiLPE-grown nine-layer structure of alternating n- and p-GaAs. Lapping angle $1.5 \pm 0.1^\circ$, p-n-selective etching in light with diluted nitric acid. The existence of the two layers of less than 1000 Å could not be proven by our present polishing and etching techniques.

thick (infinite) solution volumes were applied. By appropriate modifications of the technique an increase of the maximum stable growth rate is to be expected.

In another experiment using a cooling rate of $4^\circ\text{C} \cdot \text{h}^{-1}$ and otherwise similar conditions, a nine-layer structure was prepared with dipping times of 30, 30, 1, 1, 30, 30 min, 16 and 16 sec, and finally 30 min for the alternating n- and p-GaAs growth solutions. The result shown in fig. 6 demonstrates relatively

straight and sharp interfaces and a thickness reproducibility of about 10% for the five 30-min layers of the average thickness of $4.7 \mu\text{m}$. Not shown on this photograph is the rounded edge of about 0.6 mm around the substrate. The significance of this effect is obviously minimized when larger substrate areas are used. Meniscus lines [12] have not been detected so far and are not expected since the liquid layer remaining on the substrates in the B position prevents the "stick-slip" motion of the edge of the next solution.

Work with substrates in the A position is in progress and will show whether meniscus lines will form on "dry" substrates.

The plateaus on the layer grown from the remaining liquid layer after furnace shut-off are not representative for the surface during LPE layer deposition at high temperatures. The final mirror-like surfaces show in the Nomarski microscope faint growth hillocks which, according to Talysurf measurements, are $500 \pm 100 \text{ \AA}$ high and have a diameter of about $0.3 \pm 0.1 \text{ mm}$.

5. Conclusions

Results of first experiments demonstrate the potential of the MultiLPE technique for reproducible epitaxial deposition of a number of semiconductor layers of fixed sequences. Modifications of the double-screw technique or other topologies allow for external control of the layer sequence. In addition to the known high performance of LPE-grown devices, several problems of common graphite slider systems like layer scratching, graphite particles and meniscus lines are overcome. Large batch processing of layer structures required for fabrication of devices like LED's or III-V solar cells, lasers, and microwave diodes can be envisaged. Factors controlling the nucleation and growth mechanisms and especially the initial growth-rate transient have to be investigated in order to prepare large-area continuous layers of thicknesses of the order of 100 \AA .

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