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Liquid phase epitaxy of GaN on MOCVD GaN/sapphire and HVPE free-standing substrates under high nitrogen pressure

M. Bockowski[1], P. Strak[2], P. Kempisty[2], I. Grzegory[1], B. Lucznik[*1], S. Krukowski[1], and S. Porowski[1]

[1] Institute of High Pressure Physics, PAS, Sokolowska 29/37, 01-142 Warsaw, Poland
[2] Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-672 Warsaw, Poland

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[*] Corresponding author: e-mail bocian@unipress.waw.pl

Results of liquid phase epitaxy of GaN on MOCVD sapphire/GaN and HVPE free-standing GaN substrates by high pressure solution method are presented. The finite element calculation using experimentally measured temperatures is used for modeling the convective transport in the liquid gallium. The influence of a baffle and thermal conductivity of the various seeds for convection in liquid metal is analyzed in details.

1 Introduction It is well known that High Pressure Solution (HPS) growth method allows obtaining the GaN crystals (spontaneously grown hexagonal platelets) with the lowest dislocation density of 10^2 cm^{-2}. Recently, the liquid phase epitaxy of GaN on various seeds (pressure grown GaN crystals, sapphire/GaN templates, SiC) by HPS method was examined [1,2]. A new design, applied for directional crystallization was based on the use of a crucible with a baffle plate [2]. It allowed the formation of a uniform, flat crystallization front on the substrate and consequently to maintain a flat GaN surface during a long crystallization run. However, the main problem in this crystallization was the slow growth rate in the *c*-direction (1-2 μm/h). In order to explain the reason for the low growth rate the finite element calculation has been implemented for modeling the convective transport in liquid gallium. In this paper the stream lines, convectional flow velocity vectors and isotherm lines in liquid metal have been determined and demonstrated, based on experimentally measured temperatures during liquid phase epitaxy of GaN on the MOCVD sapphire/GaN templates and HVPE free-standing substrates. The effect of the baffle for convection in liquid metal has been analyzed. The influence of seed's thermal conductivity for distribution of convectional rolls in the liquid gallium has been described. In order to clarify the influence of seed's thermal conductivity, the SiC crystal (due to its high thermal conductivity) has also been considered for the computation.

2 Experimental

2.1 Set up The crystal growth experiments were carried out in the high pressure-high temperature apparatus at the same pressure-time conditions (nitrogen pressure 1 GPa and crystallization time 50 h). The sapphire/GaN MOCVD templates with diameters of 1 inch and 435 μm thick and HVPE free-standing crystals with diameters of 1 inch and thickness of about 500 μm were used as substrates (seeds). For HVPE crystals the mechanical polishing and Reactive Ion Etching were used to prepare their Ga-polar surfaces.

Figure 1 shows the scheme of experimental arrangement examined. The positions of thermocouples and correspond ing temperatures measured during the growth processes are indicated. The positive temperature gradient along the vertical direction of the crucible was applied. Then, the nitrogen was dissolved in the hot part of the liquid metal and transported to the cold end where the crystal growth occurred. The concentric graphite tube was located in the graphite crucible. This tube allowed fixing the seed at the bottom of the crucible. In the crucible the graphite baffle plate sustained by a graphite stick and positioned 2

mm above the seed was placed. The baffle opening was 22%.

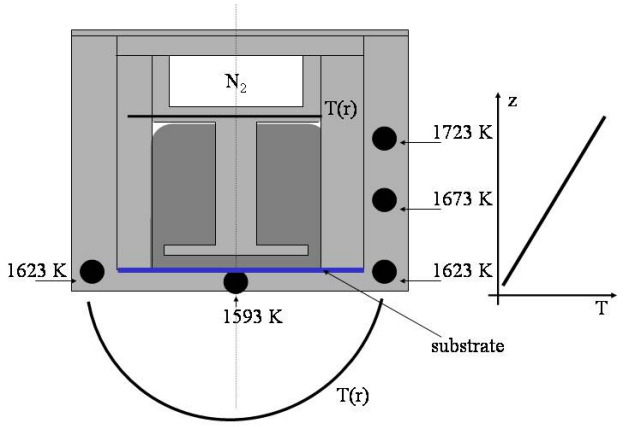

Figure 1 Crucible with the special tube, gallium, seed and with the graphite baffle plate positioned close to the seed. The positions of thermocouples and corresponding temperatures as well as axial and radial temperature distributions are marked.

2.2 Computation The analysis of the convective transport in the gallium at two-dimensional approximation for the configurations presented above was carried out with FIDAP 8.5 supplied by Fluent Inc. The convectional flow velocity in the gallium and the temperature distribution in the liquid, in the seed and in the crucible wall were determined. One considered Ga as the incompressible, viscous and Newtonian fluid, where the density changes were produced only by the temperature changes. The boundary conditions were fixed by temperatures measured in five points (see Fig. 1). The vertical temperature distribution was approximated as linear and the radial temperature distribution at the bottom of the crucible as parabolic (see Fig. 1). The radial temperature distribution on the crucible's top was assumed as constant (see Fig. 1). This assumption bases on the temperature measurements (on the crucible's top) carried out a few years ago for the similar experimental configuration. The mesh composed of 41000 elements was introduced. Assuming the laminar flow in gallium the set of Navier-Stokes equations (continuity, momentum balance and energy balance equations for Ga) was solved in order to find stationary and time independent solutions. The computation details and material properties used in simulations are presented in Ref. [3].

3 Results and discussion After 50 h of crystallization runs 50 μm thick GaN layers were obtained, both on the sapphire/GaN MOCVD template and HVPE free-standing crystal. For these two cases the flat GaN surface was obtained and one could observe the macrosteps moved from the center of the seed to its sides. Figs. 2a and b represent the stream lines and convectional velocity vectors in gallium for the examined configuration with 1 inch MOCVD sapphire/GaN template as seed. One can see two

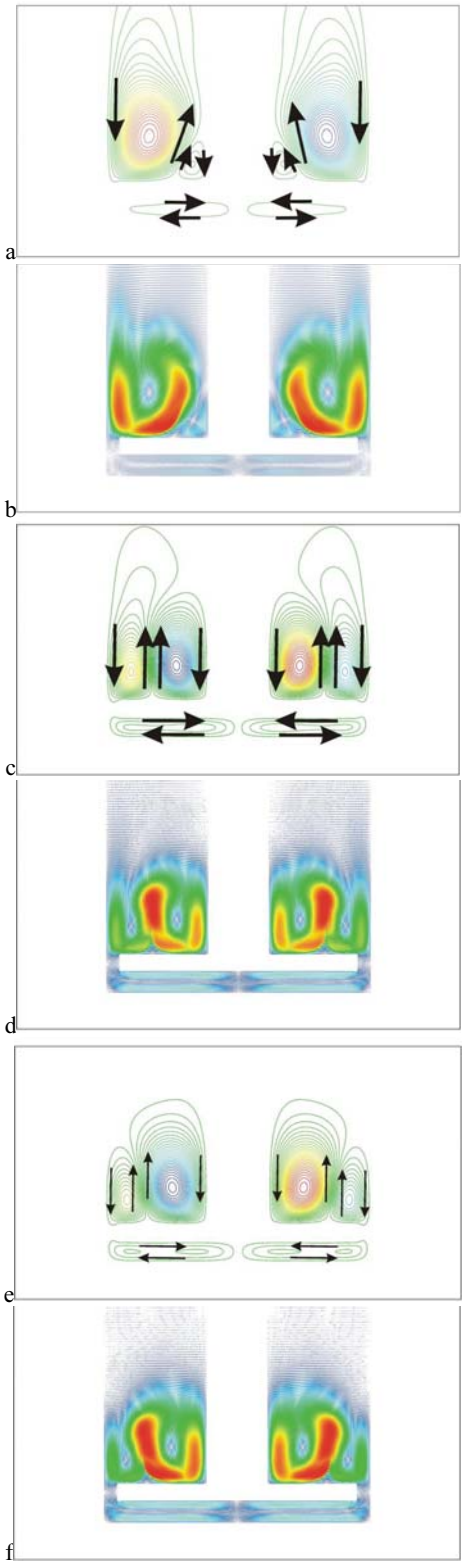

Figure 2 Stream lines with directions of rotation marked and convectional flow velocities vectors in gallium for the examined configuration with a) and b) MOCVD sapphire/GaN template, c) and d) HVPE free-standing GaN, e) and f) SiC crystal.

big convectional rolls separated one from another by the graphite stick. These rolls do not reach the bottom of the crucible because they are separated from the seed by the baffle. Close to the baffle and the stick one can see two very small rolls of low convectional velocity-0.17 mm/s. The maximum velocity for the convectional flow above the baffle is 1.3 mm/s. The maximum values are just close to the baffle (red region). Under the baffle the convection is very weak; the maximum flow velocities in two rolls achieve 0.2 mm/s. The gallium flows along the baffle to the center, then comes downwards and backs along the substrate to the sides of the crucible.

The change of the substrates can modify the distribution of the stream lines. Figures 2c and d and also e and f represent the stream lines and convectional flow in gallium with the GaN and SiC crystals as seeds, respectively. Although, under the baffle the rolls' distribution does not change and the maximum flow velocities again achieve 0.2 mm/s. Some important changes are observed above the baffle. These small rolls close to the baffle and stick have become bigger. They are the biggest for SiC crystal as substrate. The maximum velocity of the convectional flow with the GaN and SiC crystals as seeds is 1 mm/s and the maximum is placed significantly above the baffle.

The common feature of the computation (with three kinds of substrates) is that under the baffle the convectional flow is very weak and the maximum convectional flow velocity is always 0.2 mm/s. Thus the baffle plate reduces the convectional flow close to the seed. The maximum flow velocity over the baffle is 1 mm/s or more. It seems the N atoms are dispersed on the baffle and by the sides (opening areas) they are supplied below the baffle to the seed region, where their velocity is relatively low and by weak convection process they are transported to the seed. Due to a very low convectional flow velocity, the growth is macroscopically stable and flat but the rate is slow 1-2 μm/h. The direction of rolls rotation below the baffle is conformed to typical physical intuition. Due to the radial temperature gradient with cooler point at the crucible's centre, nitrogen is transported in liquid metal by two symmetrical rolls through the geometrical centre of gallium to the bottom of the crucible and then came up at the sides. There are, however, some rolls above the baffle that turn in opposite direction. A shape, size and distribution of rolls over the baffle depend on the substrate used, strictly on its thermal conductivity. The sapphire template has low thermal conductivity, of the order of 5 W/m·K at growth temperature [3]. In this case, above the baffle the liquid flows downwards at the crucible wall and upwards close to the graphite stick close to the center, thus against physical intuition. One can imagine that this seed cut off the influence of radial gradient for big mass of liquid gallium. GaN has the thermal conductivity coefficient higher than sapphire and comparable to that of graphite (24 W/m·K [4]). The main flow over the baffle is still like for sapphire, but one can observe quite big rolls turning in opposite direction (see Fig. 2c). For SiC that has the highest thermal conductivity (40 W/m·K [5]) the main flow is downwards close to the crucible center. SiC does not cut off the influence of radial gradient for mass of liquid gallium placed above the baffle. Fig. 3a presents the isotherm lines under the baffle for configuration with GaN/sapphire template as seed (the same picture is observed for GaN crystal). The isotherm lines are not flat. They start to fall at the interface between graphite and gallium and then push up at the center. The isotherm lines are concentrated in the substrate and in the baffle. They are "pushed away" from the baffle by the stick. The temperature of the substrate is not constant. There are two minima: at the center and at the sides of the seed. In spite of sinusoidal form of isotherms close to the substrate the flat growth was observed. In a case of lack of the baffle, the isotherm lines are always parabolic [3]. Their cold point is at the center of the crystal. Consequently, as a result of crystallization process the central hillock was observed [1]. Figure 3b shows the isotherm lines for configuration with SiC as seed. The behavior of the isotherms in gallium between the seed and the baffle is similar; they are curved and at the crucible center they become convex. For SiC, however, the isotherms are absolutely not concentrated in it. The boundary of SiC substrate is presented in Fig. 3b. Obviously, the temperature gradients are realized in materials of the lowest coefficient of thermal conductivity. Therefore, the concentration of isotherm lines is observed for the graphite. The perturbation of isotherm lines between the seed and baffle is caused only by the baffle system. It seems that the baffle is not necessary for obtaining flat crystallization front on SiC. This remark is in good agreement with experimental data. The growth of GaN on SiC crystals without the baffle was macroscopically flat. The main mechanism of crystallization on SiC was the formation of many small hillocks and their coalescence [1].

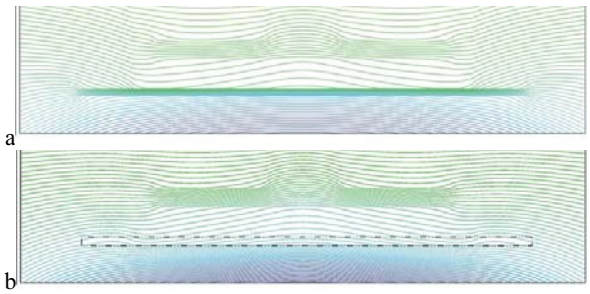

Figure 3 Isotherm lines for configuration with a) MOCVD sapphire/GaN template, b) SiC crystal. Strong concentration of isotherm lines is only observed for the template.

4 Conclusion It was shown that the baffle plate allows reducing the convectional flow close to the seed and obtaining macroscopically flat growth of GaN from the liquid phase. The influence of seed's thermal conductivity for convectional flow in liquid gallium was examined. The material of low thermal conductivity can change the rolls distribution and their direction of rotation. The use of the

seed of high thermal conductivity can result in macroscopically flat crystallization front even without the baffle plate.

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