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Growth of InN crystals with peculiar morphology by means of AP-HCVD: Computational fluid-dynamics simulation of the gas flowing in the reactor

H. Sugiura[*, 1], **N. Takahashi**[2], and **T. Nakamura**[3]

[1] Department of Optoelectronics and Nanostructure Science, Faculty of Educational Division, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan
[2] Environmental and Biotechnological Frontier Engineering, Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505, Japan
[3] Department of Materials Science and Technology, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561, Japan

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Indium nitride crystals were grown by a halide chemical vapor deposition technique under atmospheric pressure. Scanning electron microscopic observation showed that InN crystals have flower-like morphology with six petals. Computational fluid-dynamics simulation was applied to study the fluid behavior in a quartz-tube reactor used for the crystal growth. The obtained results showed that the gas flow was laminar in most areas of the reactor. No turbulent flow was observed in the vicinity of the substrate. The temperature was confirmed as less than 823 ± 0.3 K in the same area. As a result, it is deduced that the precise control of both gas flow and temperature results in the flower-like InN crystals with high reproducibility.

1 Introduction

Controllable growth of nano- and micromaterials is very important for modern materials science, which make it possible for their self-organized growth and fabrication with desirable morphology. It has been reported so far that metals, alloys and metal oxides with a variety of nano- and microstructures such as belt, tube and rod were synthesized [1–7]. However, most of them are required for a specific growth condition such as catalyst and template, so that it is important to find them for applications.

Recently, we have succeeded in the preparation of the InN crystals with flower-like morphology by means of atmospheric-pressure halide chemical vapor deposition (AP-HCVD) [8]. It has been confirmed experimentally that such flower-like crystals deposited with high reproducibility, although the growth mechanisms have been under discussion. Based on the experimental results, a key aspect of the crystal growth is expected to be a precise control of the growth conditions, in particular, gas flow and the reaction temperature. Therefore, a computational approach is a powerful tool to investigate them. In this study, therefore, we demonstrate the results of the numerical simulation of the gas flow and the temperature distribution in the quartz-tube reactor used for the crystal growth of the flower-like InN crystals.

* Corresponding author: e-mail: f5645008@ipc.shizuoka.ac.jp

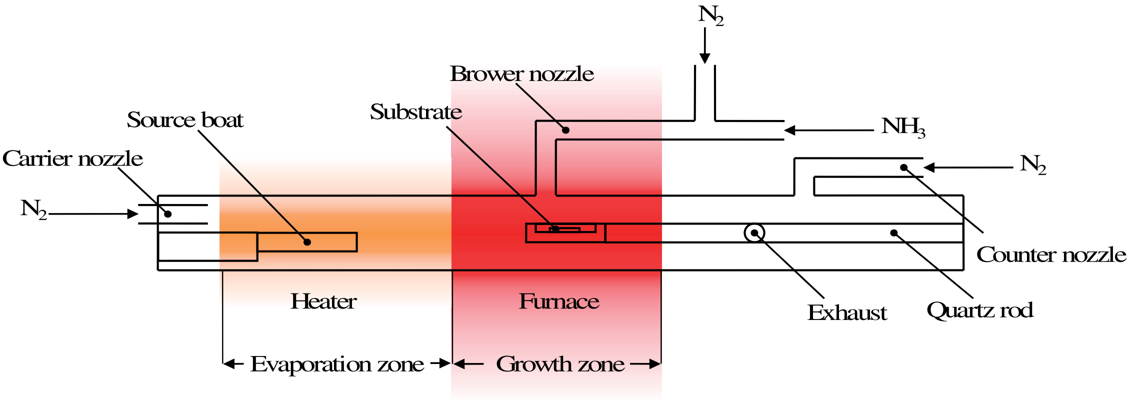


Fig. 1 (online colour at: www.pss-a.com) Schematic of the experimental setup used both for the experiments and numerical simulation.

2 Experimental

A setup shown in Fig. 1 was used both for the experiments and simulation model. The setup consisted of a horizontal quartz tube with three gas inlets and an exhaust. The quartz tube is of 1000 mm length and 34 mm ∅. N_2 carrier gas, a mixed gas of NH_3 and N_2 and N_2 counter gas were introduced from the respective inlets shown in Fig. 1. A source of $InCl_3$ in a boat was evaporated at 683 K, and then supplied to the growth zone of the quartz tube by purified N_2 carrier gas at a flow rate of 500 sccm. The mixed gas, where the NH_3 and N_2 flow rates are 170 and 80 sccm, respectively, was preheated prior to supply to the growth zone. N_2 gas was introduced into the quartz tube as a counter gas at a rate of 250 sccm. The flower-like InN crystals were grown at 823 K under atmospheric pressure on the Si(100) substrate of size $10 \times 10 \times 0.5$ mm^3 placed on the quartz rod of 8.0 mm ∅ at the center of the furnace of 300 mm in length that was just below the blower nozzle of the mixed gas.

A commercial program SCRYU/Tetra (Version 6) for the computational fluid dynamics (CFD) was used for the simulation of the gas flow and the temperature distribution, in which the governing equations used are those of continuity, momentum conservation, and energy conservation. The thermal boundary condition considered is an isothermal wall to understand the heat conduction on the gas flow inside the reactor. The finite-volume method is employed to solve the basic equations. The flowing gases were treated as a compressible fluid taking account of the density variation in the fluid under the gravitational field. The experimental conditions obtained for the flower-like crystal growth were used for the numerical simulation.

3 Results and discussion

A typical SEM micrograph of the InN crystals prepared by the AP-HCVD is shown in Fig. 2. It is obvious that the crystals have a specific morphology like a flower with six petals. The flower-like crystals were formed on the whole area of the Si(100) surface.

Figure 3 shows the simulated temperature distribution in the quartz tube of the setup during the reaction. As is seen in Fig. 3a, the gas temperature in the vicinity of the substrate is highly uniform, the difference is less than 0.3 K. Figure 3b is also confirmed by the fact that there is little influence on the temperature distribution in the vicinity of the substrate. At both sides of the furnace, on the other hand, natural convection is observed. A similar phenomenon has been reported for the simulation of the thermal CVD process at high growth temperature [9].

In order to investigate the effect of blower-gas temperature, the simulation was carried out by assuming cold and heated gas tubes that introduce the blower gas of the mixed NH_3 and N_2 (Fig. 3b and c). It should be noted that for the heated gas tube the blower gas has little influence on the substrate temperature, Original Paper

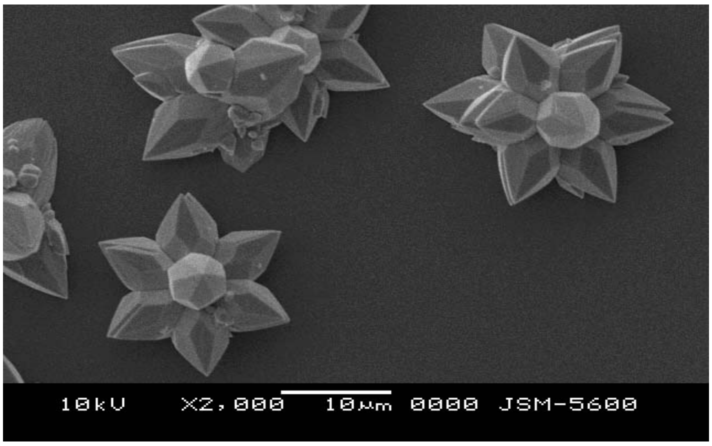


Fig. 2 A typical SEM micrograph of the InN crystals with flower-like morphology grown by means of AP-HCVD.

while for the cold-gas tube the temperature in the vicinity of the substrate is not only cooled to 772.9–773.4 K but is also nonuniform. The big difference in the case of the nonheated gas should leads to an absence of reproducibility. It is therefore suggested that using preheated gas is useful.

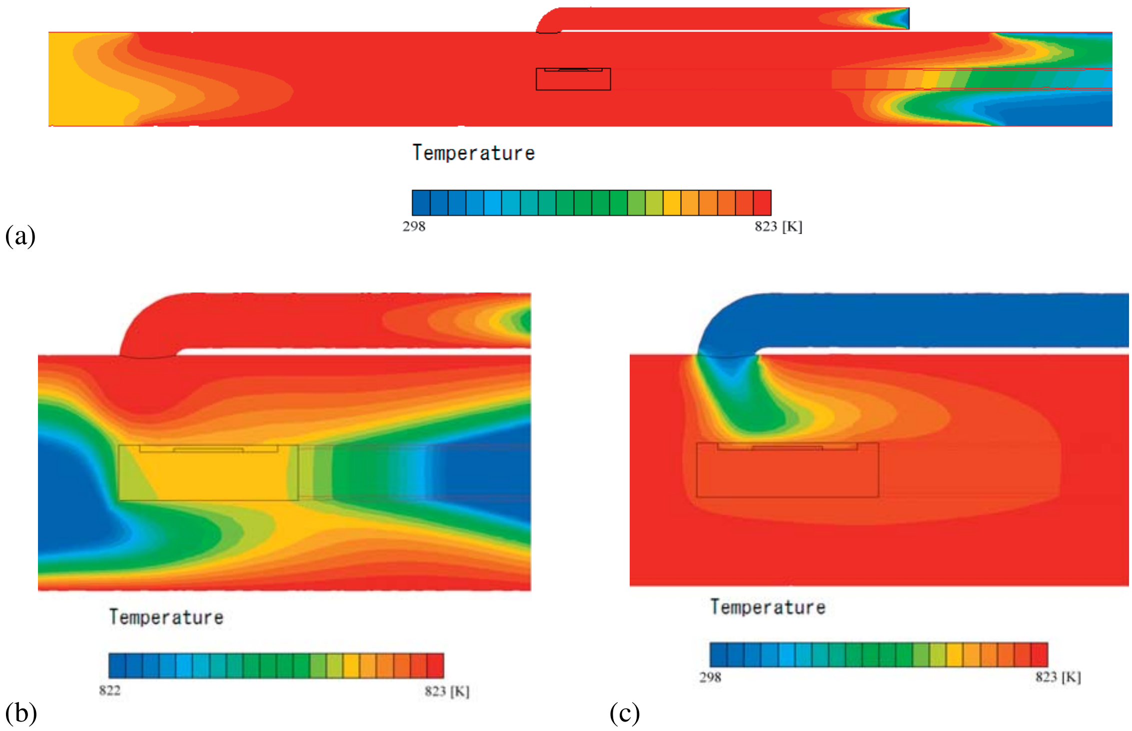
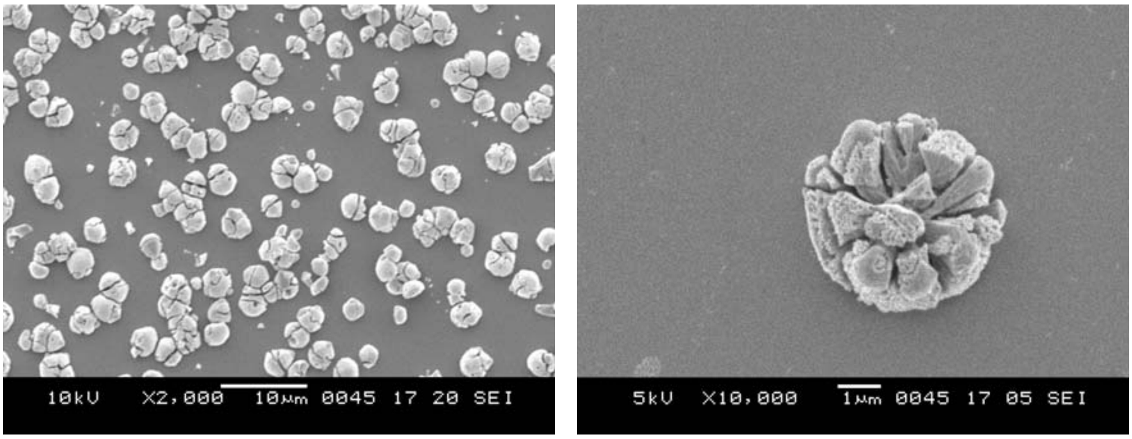


Fig. 3 (online colour at: www.pss-a.com) Temperature distributions in the quartz tube of the setup: (a) in all parts of the furnace area, (b) magnification and detailed distribution of the substrate area, and (c) magnification of the substrate area simulated in the case of nonheated blower gas assuming that the blower nozzle is outside of the furnace.



(a) (b)

Fig. 4 SEM micrograph of the InN crystals grown at 773.0 K: (a) low magnification, and (b) high magnification.

Based on the simulated results described above, the experiments of InN crystal growth at 773.0 K were carried out (Fig. 4). As is seen in Fig. 4, the SEM micrograph does not show that crystals deposited have flower-like structure.

Figure 5 shows the velocity vectors of gas flow in the quartz tube of the setup. Each vector stands for both flow velocity and direction. As is seen in the whole view, the gas flow in most of the area is laminar and the maximum of the flow velocity is of 0.646 m/s. The calculated value of Re = 789.98, which was obtained using the flow velocity 0.646 m/s and the viscosity and density of the dominant N_2 gas, implies laminar gas flow in the quartz reactor tube.

At a close look in the vicinity of the substrate (Fig. 5b), the gas flow above the substrate is laminar as well, despite the fact that there is the inlet of blower gas near the substrate, and the velocity is in the range of 0.04 – 0.06 m/s. Although the turbulence is slightly observed by the partially occluded carrier gas due to forced convection, there was no significant influence on the gas flow in the vicinity of the substrate. The surface current consists of two kinds of gases. One is the carrier gas including the $InCl_3$, which partially flows on the substrate surface after impingement at the top of the quartz rod, and the other is the blower gas including the NH_3. Therefore, it is deduced that the laminar surface gas flow produces the reproducibility of the formation of the flower-like InN crystals. This may be supported by the findings of Hirako et al. [10]. They have reported the simulated results of the two-flow MOCVD system developed by Nakamura et al. [11] using computational analysis, and concluded that backward flow on the substrate surface is caused by too strong a subflow pressure block and dilute material gases, which affects the quality of the GaN layers. In contrast to this result, ours showed that the blower gas prevents N_2-diluted $InCl_3$ gas from leaving the substrate. Plots of $InCl_3$ concentration, shown in Fig. 6, support this statement. The $InCl_3$ concentration is maintained virtually constant from the center point of the substrate surface to the upper side for 4 mm, and subsequently decreases. This means that both $InCl_3$ and NH_3 source gases are well mixed just on the substrate surface.

4 Conclusions

A computational fluid-dynamics simulation has been carried out for the formation of the InN crystals with flower-like morphology on Si(100) substrate by means of a chemical vapor deposition technique under atmospheric pressure. The simulated temperature was highly uniform in the vicinity of the substrate, which was attained both by the design of the reactor and the respective gas flow rates. In the reactor used in this study the temperature was 823 ± 0.3 K when the blower was preheated. When cold

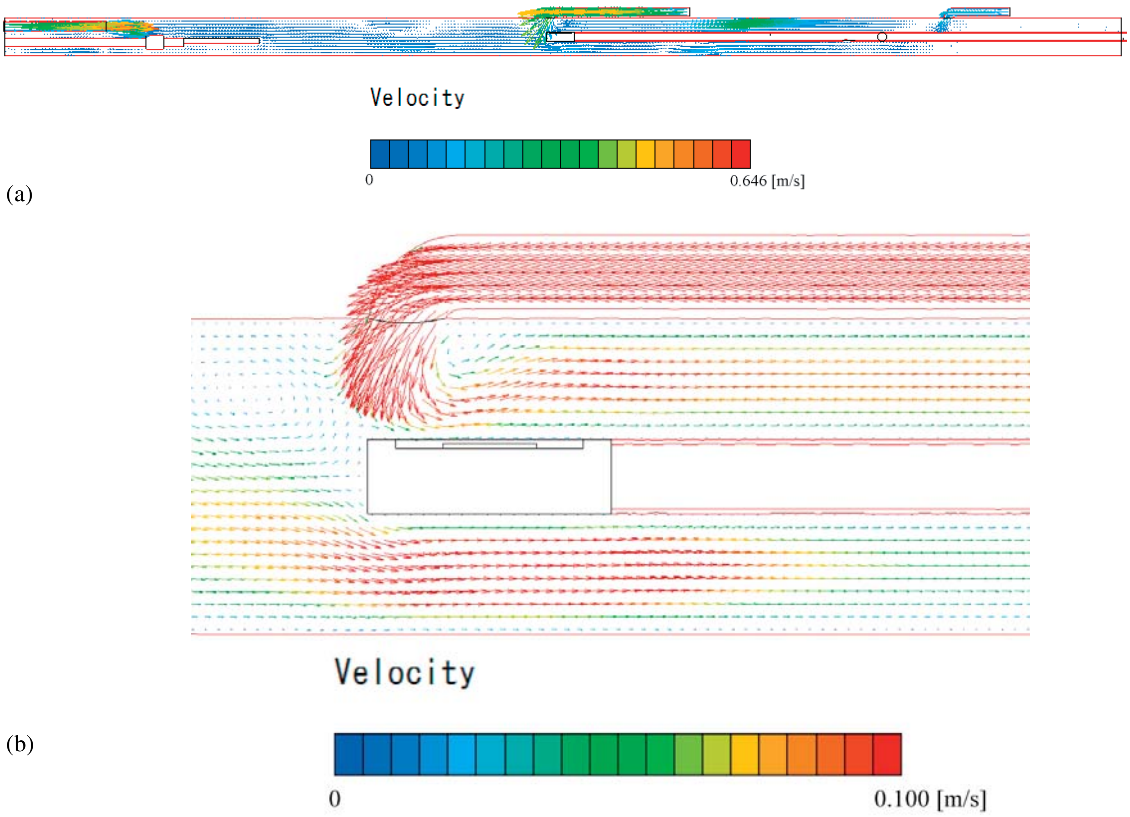


Fig. 5 (online colour at: www.pss-a.com) Velocity vectors in the experimental setup: (a) overall view, and (b) magnification and detailed illustration of the substrate area.

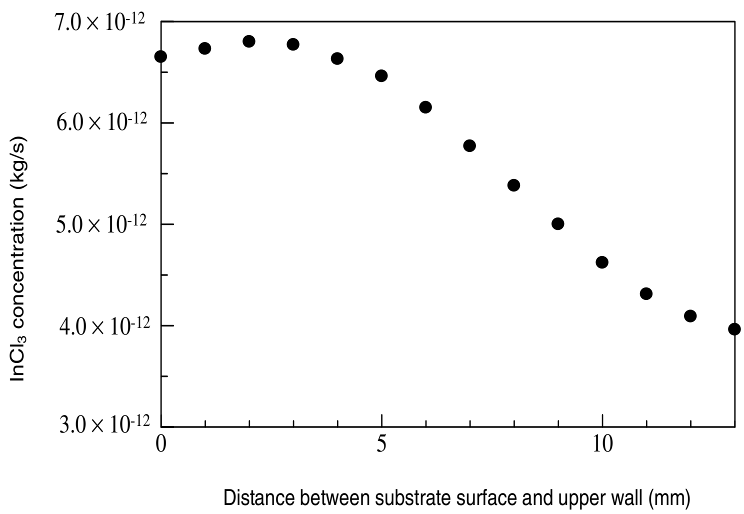


Fig. 6 Plots of $InCl_3$ concentration from the center point of the substrate surface to the upper wall.

blower gas was introduced, on the other hand, no formation of the flower-like crystals was observed experimentally, in accordance with the fact that the simulation gave a reduced temperature of 773.0 K. Also, it should be noticed that the well-controlled laminar flow occurs just on the substrate at the optimum flow rate balance of the respective gases.

It is, therefore, concluded that not only the precise control of the flow rate of respective gases introduced from three independent inlets but also the design of the reactor used are very important for the preparation of the flower-like InN crystals.

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