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Transport Processes in the Fabrication of Thin Films by Chemical Vapor Deposition

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Abstract - Chemical vapor deposition (CVD), which involves deposition of solid materials on a heated surface due to the chemical reaction of gases, is used to fabricate thin films that are of interest in the semiconductor industry and to coat surfaces for enhanced wear and temperature resistance. The quality and uniformity of the thin films, along with the rate of deposition, are of particular interest in electronic and optical applications. The flow and heat and mass transfer, along with chemical reactions, determine the film quality as well as the deposition rate. This paper is focused on the basic transport processes and presents results on chemical vapor deposition for the fabrication of thin films. The basic aspects of the process, particularly the flow and temperature distributions, for an impingement type reactor with a rotating base are first studied on a laboratory-scale simplified system. The characteristics of the flow and its dependence on parameters like inlet velocity and diameter, and susceptor temperature and rotational speed are investigated. This study, therefore, indicates the expected physical trends and provides inputs for the validation of numerical models. However, these experimental results consider only the flow and thermal transport, without considering the deposition process. But the study can form the basis for the choice of operating conditions for obtaining good film uniformity and high rates of deposition. Deposition is then investigated on a small, industrial, CVD reactor for the fabrication of Gallium Nitride (GaN) films. Thin film samples are obtained and examined for thickness uniformity and deposition rate for a variety of operating conditions. Results are presented for a few samples to indicate the basic trends that agree with the earlier findings from the lab study on the flow. It is found that increase in deposition rate often comes at the expense of film quality and, therefore, optimization must be undertaken to achieve high-quality films with acceptable deposition rates.

***Keywords*:** Thin films, fabrication, CVD, chemical reactions, Gallium Nitride, transport processes, deposition, mass transfer

1. Introduction

An important manufacturing process that is used for the fabrication of thin films needed for electronic and optical materials is chemical vapor deposition (CVD), in which the chemical reactions of gases lead to the deposition of a desired solid material on to a surface. The deposition occurs on the surface of a heated wafer or substrate. Reaction by-products are then removed by carrier gases. The heat input supplies the energy needed for the reactions, which occur in the gases as well as at the surface. The transport processes, along with chemical reactions, affect the deposition process. Interest lies in obtaining high deposition rates and high film quality, as indicated by thickness uniformity, defects and crystalline structure. The film thickness generally ranges from a few nanometers to tens of microns. Because of the large area film coverage and excellent blanketing capability, CVD has a wide range of applications where thin coatings of high purity are required, such as semiconductor devices, protective coatings, solar cells, and photonics [1].

Figure 1 (a) shows the basic processes involved in the deposition of silicon in a horizontal CVD reactor. The precursors, which include silane (SiH_4) and oxygen, along with carrier gases, enter the reactor and undergo chemical reactions in the reactor and at the surface. Various stages of molecules splitting, or adsorption, reaction to form new molecules and release of new molecules and energy, or desorption, are shown. The new solid crystalline material deposits on to the substrate and grows with time. Finally, the carrier gases move the by-products out of the system. Many other geometries and designs of CVD systems have been used, a couple of which are shown in Figs. 1 (b) and (c). This paper considers a vertical, impingement type, CVD reactor, with a rotating base, similar to the one shown in Fig. 1 (c).

A wide variety of materials have been deposited by CVD for coating and for fabricating thin films. These materials include silicon, silicon carbide (SiC), titanium nitride (TiN), graphene, gallium nitride (GaN) and aluminum nitride (AlN).

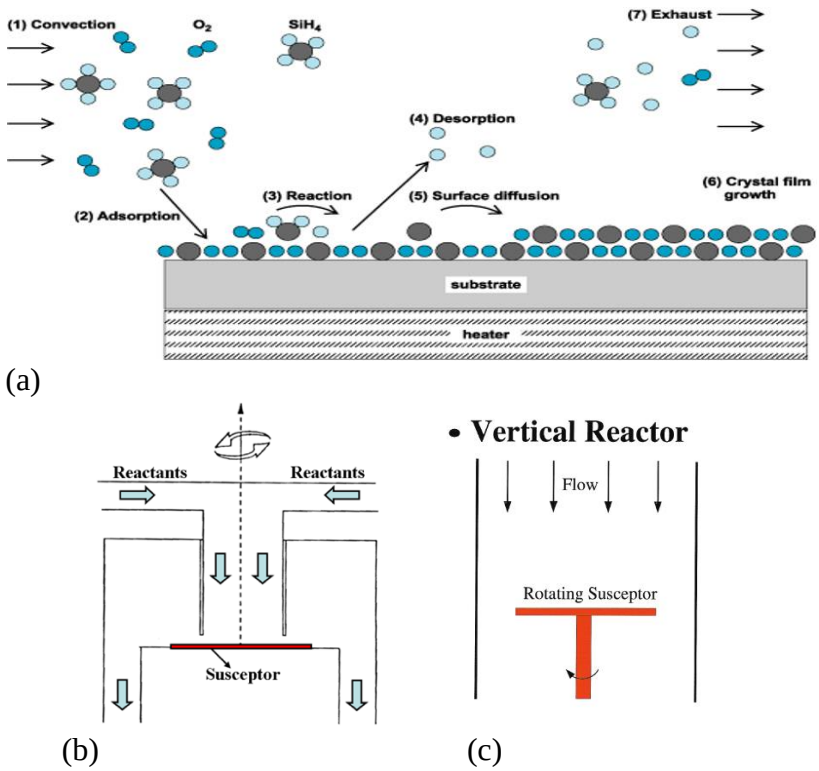


Fig. 1: (a) Basic processes involved in chemical vapor deposition in a horizontal reactor; (b) A vertical reactor with stationary susceptor; (d) A vertical, rotating susceptor, reactor.

Silicon was of particular interest and considerable work was carried out on silicon deposition [1-3]. More recently, interest has grown in materials like gallium nitride, aluminum nitride and aluminum gallium nitride. Gallium nitride is a group III/V semiconductor compound, where III and V refer to groups in the periodic table and thus to the sources of gallium and nitrogen in GaN. The semiconductors based on GaN allow the production of high-powered transmitters, light emitting diodes, transistors, and other optoelectronic components [4, 5]. The deposition process and the characteristics of the thin film are determined by the design and the operating conditions.

This paper focuses on the deposition of GaN for the fabrication of thin films. The inlet flow includes the precursor gases for which Trimethylgallium or TMGa is commonly used, ammonia, NH_3, which reacts with the precursor gases, and the carrier gases, which are typically composed of nitrogen, N_2, and hydrogen, H_2. As mentioned earlier, the substrate is heated to supply the energy needed for the reactions. The chemical kinetics involved in the process are a strong function of the temperature and have an Arrhenius equation dependence [6]. At low temperatures ($T < 600\ ^oC$), the process is limited by reactions at the surface due to the low energy levels available. At high temperatures ($T > 1400\ ^oC$), the precursors get depleted, limiting the deposition. In the medium range (800 – 1200 ^oC), the process is mainly limited by the transport of the gases.

2. Experimental Systems

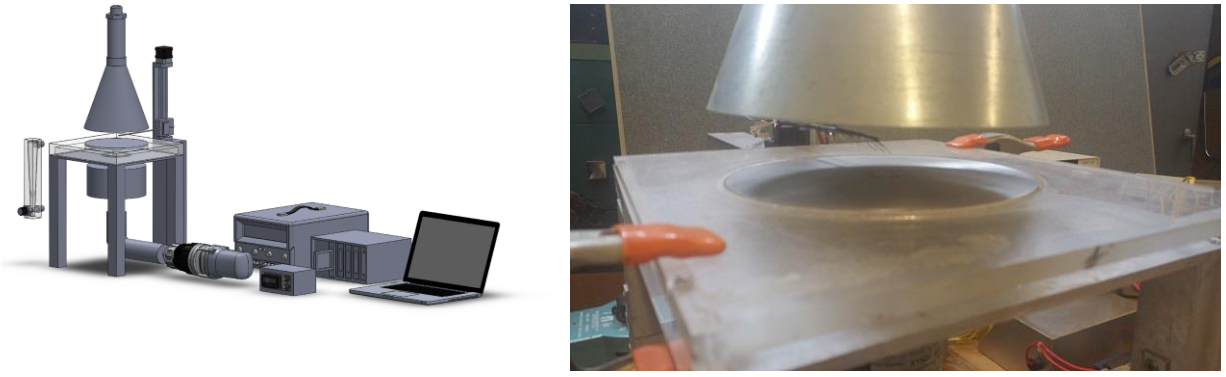
Two separate experimental systems are considered for the impingement type, rotating susceptor, CVD reactor. The first one is a simplified laboratory model to study the heat transfer and fluid flow in the reactor. Air flow enters with uniform velocity and temperature through a circular inlet. A conical upper flow guide (UFG) is used to direct the flow toward the rotating base, as shown in Fig. 2. The inlet velocity, inlet diameter, height of the inlet, rotational speed and surface temperature of the base can all be varied over wide ranges [7]. The straight profile flow guide is at uniform temperature due to its small thickness and high thermal conductivity, with heat transfer due to convection and radiation from the heated

susceptor. Existing literature may be used to model this boundary and determine its temperature. The outflow is a circular opening around the rotating base, with radial outward flow.

The second experimental system is a practical, industrial, CVD reactor, as shown schematically in Fig. 3. The flow entering the reactor at the top consists of precursors and carrier gases. The upper flow guide helps in distributing the flow uniformly over the rotating susceptor. The gases react and deposit materials such as GaN in crystalline form over wafers placed on the heated rotating surface. The thickness of the thin film grows with time and the process is terminated when the desired thickness is achieved. Several substate materials such as sapphire and silicon carbide are used to grow the thin layers. Frequently, a two-step process that involves a buffer layer at low temperature followed by GaN deposition at high temperature is used in practical fabrication systems [8]. Further details on the industrial system and on the practical processes involved may be obtained from Refs. [8-11].

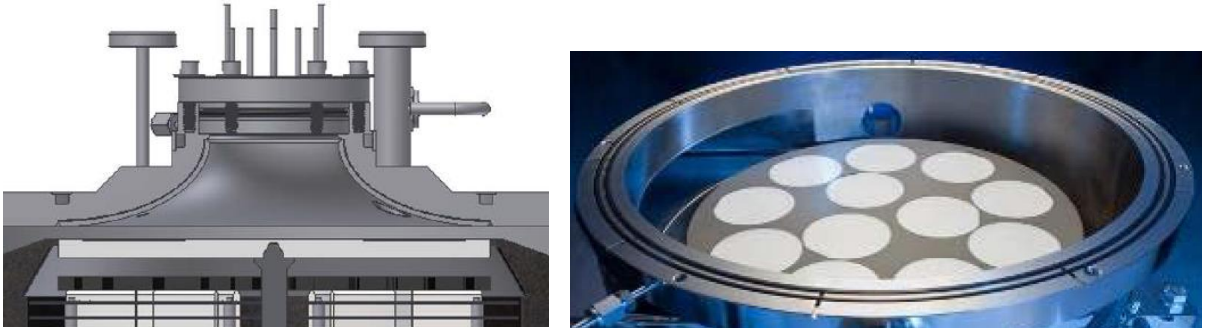
The chemical process involved in the GaN deposition process may be represented by the following chemical pathway:

$$\mathbf{2Ga + 2NH_3 = 2GaN(s) + 3H_2} \quad (1)$$



(a) (b)

Fig. 2: (a) Laboratory experimental system, and (b) Rotating base and flow guide.



(a) (b)

Fig. 3: (a) Sketch of a practical, industrial, CVD system and (b) An arrangement of wafers in a small industrial system.

However, Gallium in raw form comes in trimethygallium (TMGa) or $Ga(CH_3)_3$, which has to be broken down to Ga atom for the GaN reaction to occur. The main chemical pathway is represented by

$$\mathbf{Ga(CH_3)_3 + NH_3 = GaN(s) + 3CH_4} \quad (2)$$

Thus, methane gas is a by-product. Reactions occur in the gases as well at the surface. Due to the reactions in the gases, TMGa is broken down to Ga atom, and ammonia to Nitrogen and Hydrogen atoms. At the surface of the substrate, surface reactions lead to the Gallium and Nitrogen combining to produce the solid state GaN, which deposits on the surface. However, this is simply the basic pathway, which involves many intermediate reactions and species, thus considerably complicating the computational modelling. Substantial work has been done on modelling the complete set of chemical reactions. References [12-14] may be consulted for details on the chemistry model.

3. Results and Discussions

Flow and temperature measurements

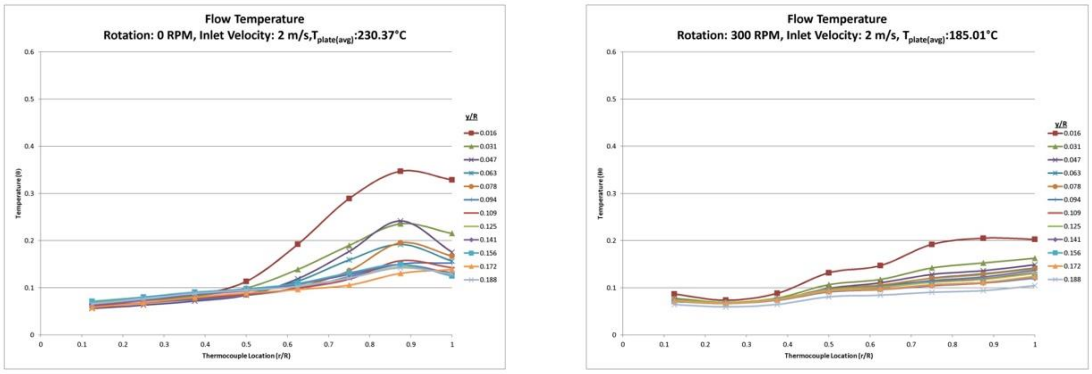
The laboratory experimental system is largely focused on the flow and thermal transport. No deposition is possible and only air at room temperature and pressure enters the chamber at the inlet. But it provides physical insight into the basic transport processes involved in the reactor. Numerical modelling can be employed to investigate the resulting deposition if the actual precursors and chemical reactions are considered. Also, experimental results on deposition are presented when the small, industrial, CVD system is considered.

An extensive study of the flow and temperature distributions in the experimental chamber is carried out. Some characteristic results are presented here. Fig. 4 shows flow visualization by means of smoke for zero rotation of the base and for rotation of 300 rpm. It is seen that a chaotic, recirculating, flow arises due to buoyancy effects with no rotation. This is replaced by a well-defined, uniform, boundary layer flow as rotation is introduced. This indicates that the deposited film is expected to be considerably more uniform when the base rotates at high speed. This trend was also seen in terms of the experimentally measured temperature distributions. The rotation causes the disturbances in the flow due to buoyancy to be reduced and a more uniform flow to arise near the rotating, heated, surface.

(a) (b)

Fig. 4: Flow visualization with smoke for (a) no rotation of the base and (b) rotation at 300 rpm.

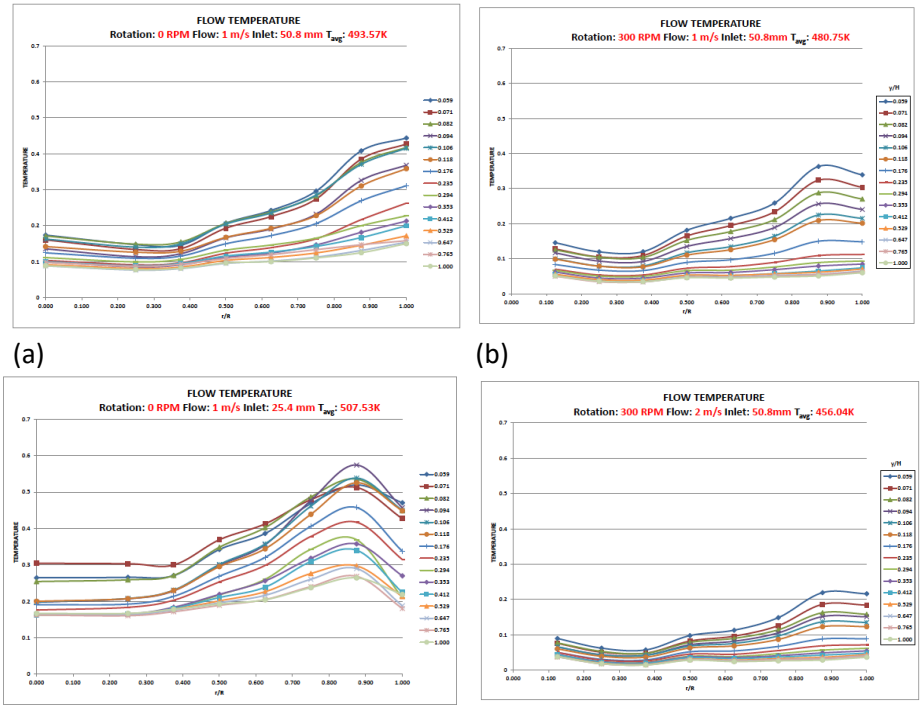
Detailed measurements of the temperature distributions in the chamber, using thermocouples with an accuracy of 0.1 ^{o}C, are shown in Fig. 5. The dimensionless temperature θ is defined as $\theta = (T - T_{\infty})/(T_{avg} - T_{\infty})$, where T_{avg} is the average susceptor temperature and T_{∞} is the ambient temperature. As seen from Figs. 5 (a) and (b), rotation of the base leads to a thinning of the boundary layer adjacent to the surface, enhanced uniformity and lowering of temperatures as the flow moves outward more rapidly. Due to thinning of the boundary layer, the heat transfer rate is also expected to increase. In practical systems, rotational speeds as high as 400 rpm and beyond are commonly used to enhance the uniformity and quality of the deposited film. Figs. 6 (a) and (b) show a similar trend at a different temperature of the rotating base. The effect of the inlet diameter is seen by comparing Figs. 6 (a) and (c). A larger diameter tends to spread the incoming flow more uniformly. This is expected to result in a more uniform thickness of the film. The effect of the inlet velocity is seen by comparing Figs. 6 (b) and (d). A larger velocity pushes the flow towards the surface and promotes uniformity. It also leads to a higher heat transfer



(a) (b)

Fig. 5: Measured temperature distributions in the chamber of the laboratory experimental system at inlet velocity 2 m/s for (a) no rotation at base temperature 230.4 ^{o}C, (b) rotational speed of 300 rpm at base temperature 185 ^{o}C.

rate. With higher velocity, the boundary layer is thinner and temperatures are somewhat lower, as expected. Since the mass flow rate is increased, a higher deposition rate is expected. The effect of buoyancy is characterized by the Richardson number Ri, which compares the buoyancy with inertia effects. It was found that buoyancy effects are important in all the cases considered. However, increase in rotational speed and the inlet velocity reduce this effect and promote uniformity at the heated surface. Similarly, higher temperatures lead to greater buoyancy effect and a more disturbed flow. These observations can be used to choose the conditions for practical reactors.

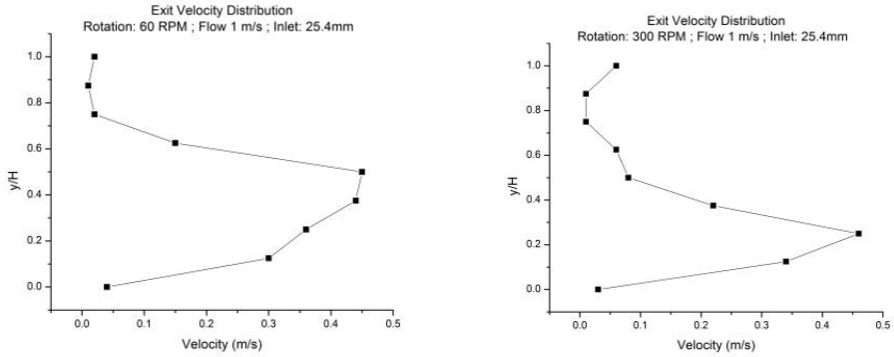


(a) (b)

(c) (d)

Fig. 6: Measured temperature distributions in the chamber of the laboratory experimental system for various operating conditions, as indicated in the figures.

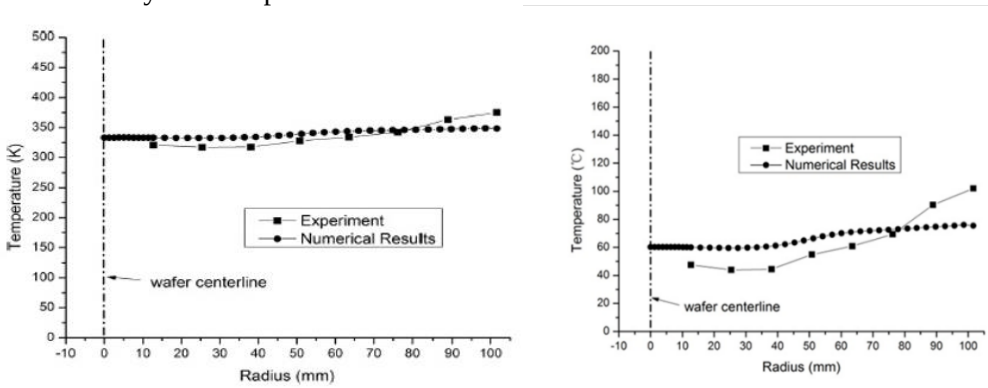
Figure 7 shows the measured exit velocity at the opening located circumferentially at the base. With rotation, the velocities are larger and the boundary layer is thinner, as seen earlier. All these results point to the need of reducing disturbances and enhancing the uniformity of the flow near the base, or susceptor. A thinner boundary layer would lead to an increased heat and mass transfer and thus a greater deposition rate. A simple numerical modelling of the flow was also undertaken using a commercially available software. Figure 8 shows a comparison between numerical and experimental results on the temperature distribution close to the heated surface, at a distance of 0.8 mm above the rotating plate. Both zero rotation and a rotational speed of 60 rpm indicate close agreement, lending support to the model.



(a) (b)

Fig. 7: Measured exit velocity with rotational speeds of (a) 60 and (b) 300 rpm.

All these results indicated the dependence of the flow on the inlet diameter and velocity, rotational speed, and temperature of the base. It is obviously important to reduce the buoyancy effects to obtain a less disturbed flow in the chamber by increasing the inlet velocity and the rotational speed and decreasing the temperature. However, the temperature is also critical for the chemical reactions and the appropriate value is needed to obtain high deposition rate. These experiments indicate the basic nature of the flow and may be used for validating numerical models. The results can also be used for choosing operating conditions to promote uniform thickness of the deposited film and high deposition rates. This was done and the results obtained on a small industrial system are presented next.



(a) (b)

Fig. 8: Calculated and measured temperature variation 0.8 mm above the heated surface at inlet velocity of 1 m/s with (a) no rotation and (b) rotational speed of 60 rpm.

Experimental results on an industrial system

A commercial CVD reactor, as shown in Fig. 3, was used for experimentation on GaN thin film deposition. The results for several samples were obtained. Each sample was deposited under specific conditions. The deposition process for each

sample lasted from 1 to 2 hours. A scanning electron microscope (SEM) is used to determine the film thickness and the material structure. Atomic Force Microscopy is used to determine the local roughness and surface morphology. The inlet flow is guided by a flow channel toward the rotating susceptor, which is heated by electrical heaters located below the surface. The inlet flow rate and composition, rotational speed, susceptor temperature and pressure can be varied. Several samples were obtained and investigated for uniformity, deposition rate and film thickness. The results for three typical samples are presented here to indicate the general trends and provide results that may be used for validating numerical simulation of this complex process. The operating conditions were chosen using the results and trends from the laboratory experimental system.

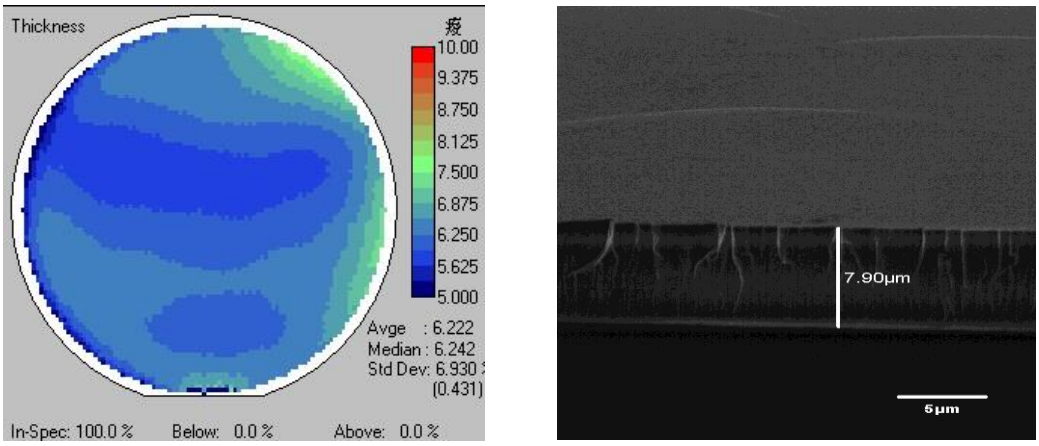
Sample A

The operating conditions employed for Sample A were the susceptor heater temperature at1040 ^{o}C or 1313K. The mass flow rate was 5.563 x 10^{3} kg/s, which gives as inlet velocity of 3.68 m/s, and the total run time was 2 hours. The pressure was 200 torr and the rotational speed was 450 rpm. Nitrogen was 41.56 % and Hydrogen and Ammonia were 29.01 % each. TMGa was 0,.42 %. The overall flow characteristics are largely affected by the inlet flow and the rotational speed. The effects of buoyancy were determined to be small under these conditions. The flow is well-behaved, with no recirculation or chaotic flow, implying a uniform deposition on the substrate.

For this sample, the film thickness was measured by using a Nanometrics Film Thickness measurement machine. The results in terms of thickness contours are shown in Fig. 9 (a). The average thickness was obtained as 6.222 microns. The average deposition rate was numerically calculated as 3.44 microns/hour, which gives a thickness of 6.88 microns after a 2-hour deposition process. An SEM image was also obtained and the image is shown in Fig. 9 (b). The measured thickness at the center of the wafer is 7.9 microns, giving a difference of 12.9 % between the experiment and the simulation. For the operating conditions employed, the film is uniform in thickness and no significant protrusions were observed in the film.

Sample B

The operating conditions for Sample B are given in Fig. 10 (a). The susceptor rotational speed is set at 300 RPM and the susceptor heater temperature at 1040 ^{o}C or 1313K. The mass flow rate is 5.568 x 10^{3} kg/s, which gives an inlet velocity of 3.69 m/s. The total process time is 2 hours. No significant changes are seen in the contour levels from those seen in the preceding case. Deposition uniformity is indicated by the thickness contours in Fig. 10 (b). However, the deposition rate decreased to an average of 3.21 micron per hour, due to the decrease in the TMGa concentration. The average thickness was 6.147 microns. The measured film thickness was 6.42 microns and the difference between measured and predicted film thickness was obtained as 4.3 %.

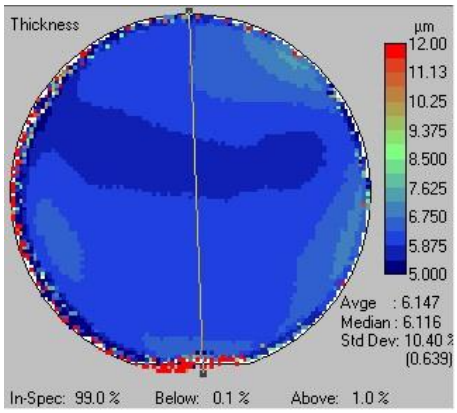


(a) (b)

Fig. 9: (a) Film thickness contours; (b) Scanning electron microscope (SEM) image for Sample A.

GaN Condition - PR07			
Pressure (Torr)	200	Nitrogen	41.49%
Rotation (RPM)	300	Hydrogen	29.05%
Heater Temp (C)	1040	Ammonia	29.05%
Inlet mass flow (kg/s)	0.005568	TMGa	0.41%

(a)



(b)

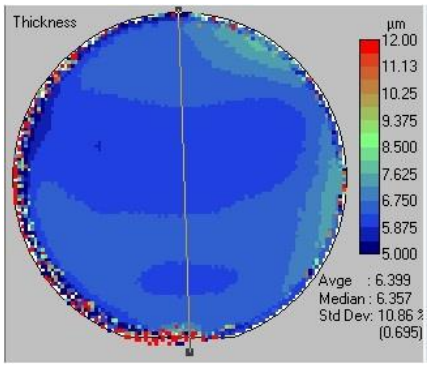
Fig. 10: Sample B: (a) Operating conditions; (b) GaN film thickness contours.

Sample C

Sample C is obtained with the conditions given in Fig. 11 (a). The mass flow rate is set at 5.563 x 10^3 kg/s, which gives an inlet velocity of 3.06 m/s. The total process time is again 2 hours. Nitrogen, Hydrogen and Ammonia flow rates were increased and the TMGa concentration was decreased, as compared to the previous sample. Decreasing TMGa causes the inlet flow velocity to drop by 0.62 m/s. No significant changes were observed in the thermal boundary layer and the flow. The flow streamlines were seen to very uniform and laminar, as in the previous samples. Since turbulence and disturbances would deteriorate the film quality, the flow rates were kept low to ensure laminar, undisturbed, flow.

GaN Condition - PR08			
Pressure (Torr)	200	Nitrogen	41.53%
Rotation (RPM)	300	Hydrogen	29.07%
Heater Temp (C)	1040	Ammonia	29.07%
Inlet mass flow (kg/s)	0.00460926	TMGa	0.33%

(a)



(b)

Fig. 11: Sample C: (a) Operating conditions; (b)GaN film thickness contours.

The decrease in the TMGa concentration results in a decrease in the deposition rate. The average deposition rate was obtained as 3.0 microns per hour. This value is lower than that for the previous sample, as expected from the decreased TMGa concentration. From the experimental thickness contours in Fig. 11 (b), the average thickness is determined to be 6.399. The difference between predicted and measured film thickness was 6.2 %. The thickness is also seen to be quite uniform. Several other samples were obtained. But the results were quite similar and are thus not included here.

The novelty of this work is that the basic nature of the flow is studied in laboratory experiments with no deposition. However, these results were successfully employed to determine the optimum conditions for deposition of high-quality films at acceptable high rates of deposition. Thus, deposition of other materials may be considered using the basic flow characteristics. The numerical models and practical deposition results are in good agreement, expanding the range of

conditions that may be considered. It is found that quality comes at the cost of deposition rate. Therefore, optimization is needed to obtain high deposition rates with films of uniform thickness and high quality.

4. Conclusions

An experimental study on the fabrication of gallium nitride thin films in a vertical, rotating base, chemical vapor deposition reactor is carried out. A simple laboratory experimental model is first employed to investigate the flow and temperature distributions in a CVD reactor. Higher rotational speeds and smaller inlet velocities are shown to lead to more uniform thermal boundary layers at the surface and thus a more uniform thickness of the film. Higher inlet velocities are seen to increase the heat transfer from the surface and are, thus, expected to increase the deposition rate. A small industrial CVD reactor is then used to obtain thin film samples under different operating conditions. A good agreement is observed between earlier simulation results and the current experimental results. It was again shown that rotational speed is an important parameter that promotes thickness uniformity as the speed is increased. An increase in pressure and gallium precursor (TMGa) concentration is found to increase the deposition rate but also to increase the film thickness nonuniformity. The temperature of the rotating surface, inlet velocity and concentration ratio are also varied. Similarly, higher inlet flow rate and greater pressure lead to larger deposition rate. But these also result in greater nonuniformity in film thickness, indicating the need to optimize with film quality and deposition rate as the two objectives.

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