Deposition of GaN by Chloride VPE and its Thermodynamic Analysis

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Abstract

The GaN thick films were deposited on sapphire substrates by the chloride vapor phase epitaxy (CVPE) technique using the $GaCl_3$-NH_3-N_2 chemistry. Thermodynamic simulations were carried out to predict the optimum process windows, and the results were compared with the experiments. A large difference in the growth temperature was observed between the calculation and the experiment, and it indicated that the growth of GaN by the CVPE technique is kinetically limited.

1. Introduction

The GaN is a promising material for the optoelectronic devices in the blue and UV spectral region. It is also a good candidate for high temperature and high frequency electronic devices[1]. The GaN films are typically deposited by vapor phase epitaxy techniques such as MOVPE (Metal-Organic Vapor Phase Epitaxy), hydride or chloride VPE, and MBE (Molecular Beam Epitaxy). Recently the high growth rate deposition techniques (e.g., hydride or chloride VPE) have been revisited by many researchers in an effort to achieve thick epitaxial substrates for GaN homoepitaxy[2,3]. These techniques, however, must be carefully applied to the GaN growth, since the crystal defects originating from the N vacancy and the high level of unintentional n-doping could be easily introduced by these techniques. The growth process needs to be very well controlled in order to produce high-quality GaN epi-layers.

In this study, the CVPE technique was utilized to deposit thick GaN films on sapphire substrates using the $GaCl_3$-NH_3-N_2 chemistry. Equilibrium calculations of the growth process were first carried out to predict the effect of process variables (e.g., the deposition

temperature, the source gas input ratio, etc.) on the equilibrium gas phase mole fractions and the deposition yield. These calculations were also performed to predict the optimum process windows. Calculated results were compared with the experimental data from actual growth runs and discussed.

2. Thermodynamic simulation

A complex thermodynamic simulation of the CVPE process was performed through calculation of equilibrium compositions of reactants and products by utilizing a stoichiometric algorithm. The simulation involved the equilibrium calculations of multi-phase, multi-component mixture with chemical reactions. The thermochemical system of this study involved 4 elements (N-H-Ga-Cl) and 3 phases (gas, liquid, and solid phases).

First, all the important chemical species which could be present in the system were thoroughly investigated, and their thermochemical data were carefully reviewed and selected from the literature[4-7]. The selected chemical species were total 24 vapor phase species and 2 condensed phase species (liquid Ga and solid GaN). Calculations were performed by varying the deposition temperature between 500 and 1500 K, and by varying the $GaCl_3/[GaCl_3 + NH_3]$ ratio between 0 and 1. The reactor pressure and the $N_2/[GaCl_3 + NH_3]$ ratio were fixed at 1 atmosphere and 5.2767, respectively. The equilibrium vapor phase mole fractions and the GaN(s) deposition yield were investigated as a function of the process variables.

3. Experimental

A conventional hot-wall horizontal reactor system was used for this study, and the schematic of the system is shown in Fig. 1. The reactor body was made of quartz and resistively heated by a tubular furnace.

$GaCl_3$ and NH_3 were used as the source gases, and N_2 was used as a carrier gas. Gas flow rates were controlled by the mass flow controllers, and the mole fraction of the $GaCl_3$ is controlled by the carrier gas (N_2) flow rate and the $GaCl_3$ bubbler temperature.

The substrates used in this study were C-plane (0001) sapphires and first cleaned by TCE (trichloro-ethylene) and ethanol two times. Substrates were further etched by H_2SO_4: H_3PO_4 (3:1) solution at 160℃ for 15 min. and rinsed by DI water for 10 min.

The substrate surface was nitridated before the GaN growth by flowing NH_3 in the reactor at the growth temperature. The $GaCl_3/NH_3$ flow ratios could be varied between 1 and 3, and the deposition temperature was varied in the range between 970 and 1040℃. The deposited films were characterized by PL, XRD, and SEM.

4. Results and Discussion

Fig. 2 shows the calculated equilibrium vapor phase mole fractions in the reactor as a function of the deposition temperature. Major vapor phase species in the reactor were found to be N_2, H_2, NH_3, GaCl, $GaCl_3$, and HCl. The $GaCl_3$ was more abundant than the GaCl below about 900 K, but became less than GaCl above 900 K.

Fig. 3 shows the GaN deposition yield as a function of the deposition temperature at various source gas input ratios. The deposition yield increases as the deposition temperature increases at a lower temperature range, but shows a maximum at about 670 K, and then rapidly decreases. The yield becomes negative (etching region) above 750 K. Varying the source gas input ratio did not change the general trend of deposition yield. The deposition yield was mostly affected by the Ga/Cl ratio in the vapor phase, as shown in Fig. 4. The vapor phase Ga/Cl ratio decreases between 500 K and 670 K where the yield increases, and it increases rapidly above 670 K where the yield of GaN(s) sharply drops.

Fig. 5 shows the experimentally measured growth rates as a function of the source gas input ratio at the deposition temperature of 1313 K. The growth rate showed a maximum value at the $GaCl_3/NH_3$ ratio of 2 (i.e., Ga/[Ga + N] = 0.67). This result was not expected by the equilibrium calculations, since the calculation showed a monotonic decrease of the yield above the Ga/[Ga + N] ratio of 0.25 (see Fig. 3). A very large difference in the deposition temperature was also observed. The experimentally optimized deposition temperatures were typically above 1123 K to obtain single crystalline films, even though the equilibrium calculations predict the dissociation of solid GaN into the vapor phase at these temperatures, leading to the etching of GaN.

These results indicate that the deposition of GaN is kinetically limited. It was believed that the dissociation of GaN goes through the following steps: GaN(s) $\rightarrow$ Ga(l) + 1/2 N_2 $\rightarrow$ Ga(g) + 1/2 N_2. The first step is the controlling step, and the activation energy of this step is so large that the GaN can stay in a meta-stable solid state even at high deposition temperatures[7,8]. The activation energy for this step can be lowered if nucleation sites (liquid gallium droplets) are artificially supplied[9], but in the typical CVPE process the liquid Ga cannot be present in the reactor. Thermal decomposition of source gases ($GaCl_3$ and NH_3) prior to the GaN formation have also high activation energies, requiring the deposition temperature typically above 900 K. These factors make the GaN deposition by CVPE technique occur far from equilibrium.

Acknowledgements

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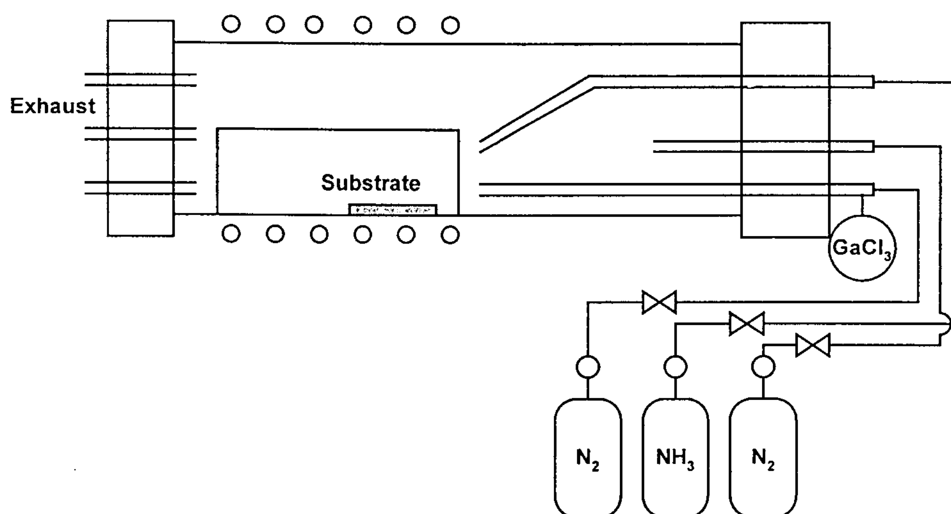

Fig. 1 Schematic diagram of the CVPE system.

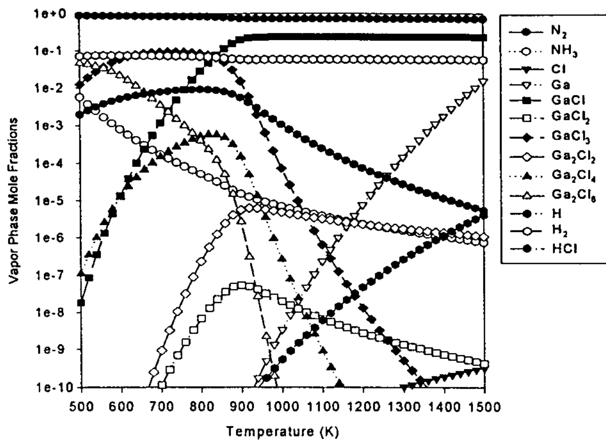

Fig. 2. Equilibrium vapor phase mole fractions of the $GaCl_3$-NH_3-N_2 system
(P_t = 1 atm; N_2 / [$GaCl_3$ + NH_3] = 5.2767; Ga / [Ga + N] = 0.67)

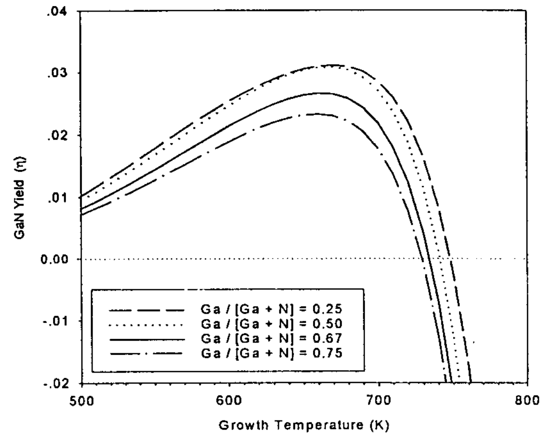

Fig. 3. Temperature effect on the GaN deposition yield
(P_t = 1 atm; N_2 / [$GaCl_3$ + NH_3] = 5.2767)

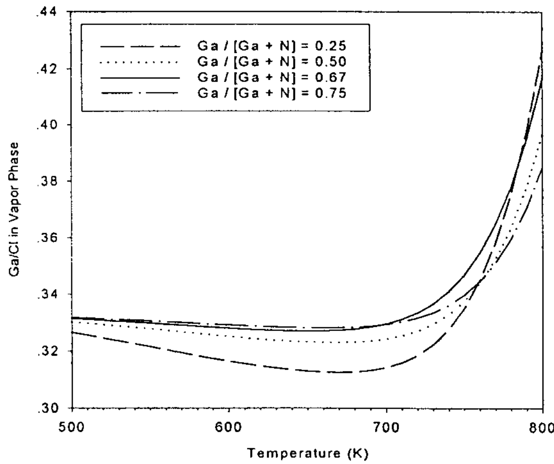

Fig. 4. Temperature effect on the Ga/Cl ratio in the vapor phase
(P_t = 1 atm; N_2 / [$GaCl_3$ + NH_3] = 5.2767)

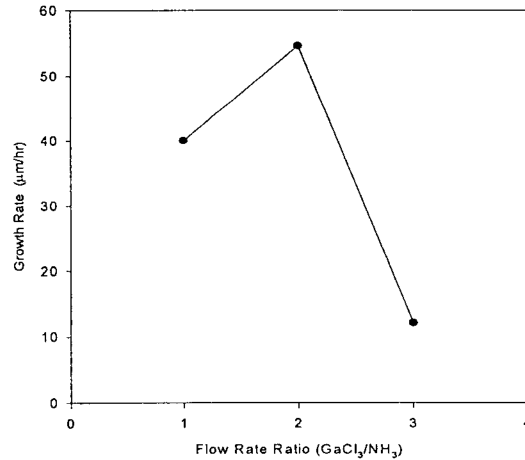

Fig. 5. Source gas flow rate ratio effect on the GaN growth rate
(P_t = 1 atm; T = 1313 K; N_2 / [$GaCl_3$ + NH_3] = 5.2767)