

Thermal Stability of MOCVD and HVPE GaN Layers in H₂, HCl, NH₃ and N₂

M. A. MASTRO¹) (a), O. M. KRYLIOUK (a), M. D. REED (a), T. J. ANDERSON (a), A. DAVYDOV (b), and A. SHAPIRO (b)

(a) *Department of Chemical Engineering, University of Florida, Gainesville, FL, USA*

(b) *Metallurgy Division, NIST, Gaithersburg, MD, USA*

(Received July 25, 2001; accepted July 30, 2001)

Subject classification: 68.55.Jk; 68.60.Dv; 81.15.Gh; S7.14

This work represents a complete study of GaN annealed in H₂, HCl, NH₃ and N₂. The GaN thermal behavior was evaluated by comparison of MOCVD and HVPE samples. The MOCVD films were found to obey a dissociative sublimation mechanism with only gaseous species forming, while the HVPE films reacted with ambient gases to form condensed Ga in addition to the gaseous species. Differences in crystal quality for MOCVD and HVPE samples resulting from the different growth mechanisms account for the observed difference. This analysis of the thermal stability of GaN is extended to include how polarity affects the thermal behavior of GaN during growth and annealing of MOCVD and HVPE films.

1. Introduction The recent development of GaN based blue light emitting diodes (LEDs) and lasers [1] and high power/high temperature electronics [2] has led to a flurry of research in the III-nitrides. The concept of thermal stability is intricately intertwined with every aspect of GaN growth and processing. Hence a detailed study of the reactivity of GaN with various ambient gases is critical to the understanding of these issues as well as the future development of complex devices [3].

On heating, GaN can undergo the following possible routes depending on the annealing conditions (Table 1): dissociative sublimation with no decomposition into the liquid phase or thermal decomposition accompanied by liquid gallium droplet formation [4–6]. By undertaking a series of evaporation experiments in various ambient gases we have observed either thermal decomposition or etching (sublimation) of GaN depending on the nature of the ambient gas, annealing temperature, and growth technique, and GaN surface morphology and polarity.

2. Experimental For comparison, HVPE and MOCVD samples of GaN were prepared at University of Florida. MOCVD is the standard method for producing thin GaN epilayers, while HVPE is a common alternative for producing GaN samples.

The growth conditions for the samples were as follows: MOCVD cold-wall horizontal reactor, HVPE hot-wall horizontal reactor; temperature: MOCVD at 850 °C, HVPE at 950 °C; pressure: MOCVD at 76 Torr, HVPE at 760 torr; V/III ratio: MOCVD 3000, HVPE 125; thickness: MOCVD, 1 μm and HVPE, 10 μm both on c-sapphire (7 × 5 mm² pieces) [7]. These samples were then annealed for 30 min in a hot wall furnace under various ambient gases from 500 to 1400 °C.

¹) Corresponding author; Tel.: 352-846-2989; Fax: 352-392-9513; e-mail: mmastro@che.ufl.edu

Table 1
GaN thermal behavior comparison of MOCVD and HVPE samples

annealing gas	growth technique	mechanism	evaporation point	comment
HCl	MOCVD	sublimation	800 °C	slight etching above 800 °C
	HVPE	decomposition	800 °C	etching above 900 °C
H ₂	MOCVD	sublimation	800 °C	completely sublimed by 900 °C
	HVPE	decomposition	800 °C	100 μm droplets at 900 °C
NH ₃	MOCVD	sublimation	small effect at 965 °C	roughens above 800 °C
	HVPE	decomposition	small effect at 965 °C	smooths above 800 °C
N ₂	MOCVD	negligible	completely stable to 1400 °C	from 40 to 760 Torr
	HVPE	decomposition	1200 °C	negligible influence of pressure

3. Results In this paper the study of GaN annealed in H₂, HCl, NH₃ and N₂, (the most common processing gases) was completed (Table 1). Additionally, the differences between MOCVD and HVPE films in these gases were compared. All films were characterized by use of AFM, AES, SEM, and EDS.

3.1 Annealing in HCl The HCl annealing study of MOCVD and HVPE films illustrates the general results found for the thermal stability of GaN.

Annealing of MOCVD GaN: A comparison of MOCVD GaN for different anneal temperatures was performed under HCl gas. As is evident from the series of SEM pictures in Figs. 1²⁾ a to c the surface of GaN is still intact at 800 °C. At 900 °C, these films begin to sublime as is seen in Figs. 1b, c where the white area is GaN, the gray one is the original GaN, and the black is the sapphire substrate. At 900 °C nearly 1/4 of the film has sublimated leaving only the substrate (black areas). At 965 °C 3/4 of the film has sublimated.

The surface of the MOCVD films has excellent structural quality and specular surfaces which possess high kinetic barriers that prevent GaN from thermally decomposing into liquid (gallium) and gas phases during the anneal. Figure 1d shows AES of MOCVD GaN annealed in HCl exhibiting slight sublimation (N and Ga loss) beginning at 800 °C. This agrees with the previous SEM/EDS results. Thus, HCl anneals of MOCVD GaN follow a dissociative sublimation route that can be expressed as the following simplified reaction:



²⁾ Colour figures are published online (www.physica-status-solidi.com).

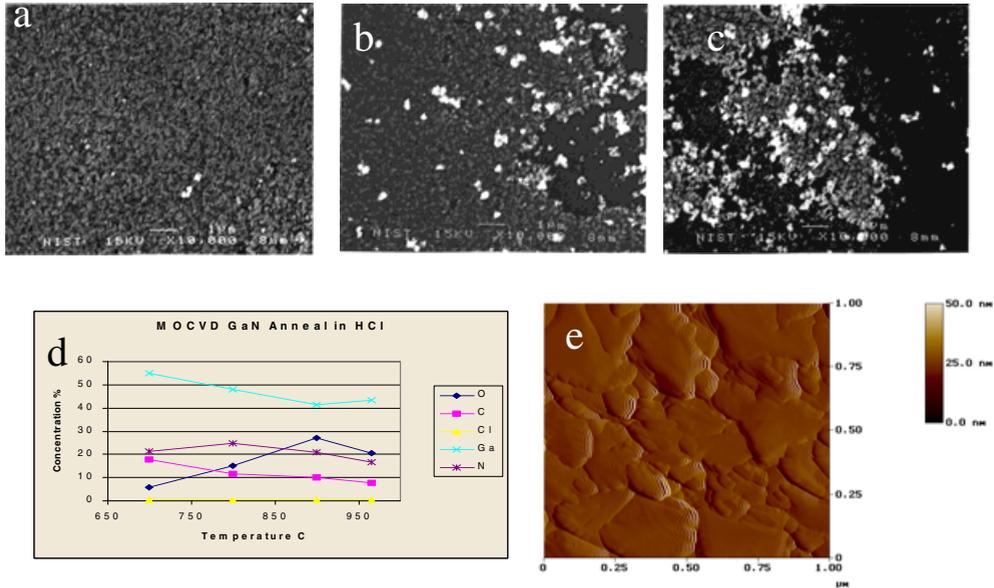
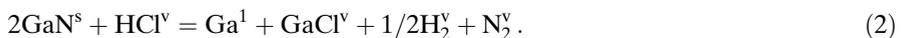


Fig. 1 (colour). MOCVD GaN annealed in HCl; SEM at a) 800, b) 900, c) 965; d) AES of MOCVD GaN annealed in HCl; e) AFM of MOCVD annealed in HCl at 900 °C

The validity of this reaction was justified by performing equilibrium closed box-type calculations for the GaN and HCl mixtures using thermodynamic data for solid GaN [4] and for all possible gas species in the Ga–N–H–Cl system [8, 9] employing Thermo-Calc software [10].

Anneal of HVPE GaN: Figure 2 a shows small droplets on top of GaN hexagonals starting to form at 800 °C. These droplets were identified as consisting of elemental gallium according to the EDS analysis. Thus, at high temperature, partial decomposition occurs for HVPE films under HCl ambient

Aside from the partial decomposition, Figs. 2a and b show that simultaneously the GaN surface is being etched, exaggerating hexagonal pyramids. In Fig. 2c, AES shows decomposition (nitrogen decrease) of the GaN at higher temperatures. A plot of AFM root mean square roughness versus annealing temperature (Fig. 2d) shows the difference between MOCVD and HVPE films. MOCVD films begin to roughen above 900 °C as the etching occurs. Figure 2d shows that the HVPE films begin to roughen at 800 °C. The reaction of HVPE GaN film with the HCl gas can be expressed as the following decomposition route:



3.2 Annealing in H₂ For MOCVD GaN films annealed in H₂ up to 700 °C, no change in film composition or morphology is observed. Annealing at 900 °C resulted in the complete sublimation of GaN film. On the contrary, HVPE GaN shows thermal decomposition at as low as 800 °C, evident by the small size Ga droplets. The sublima-

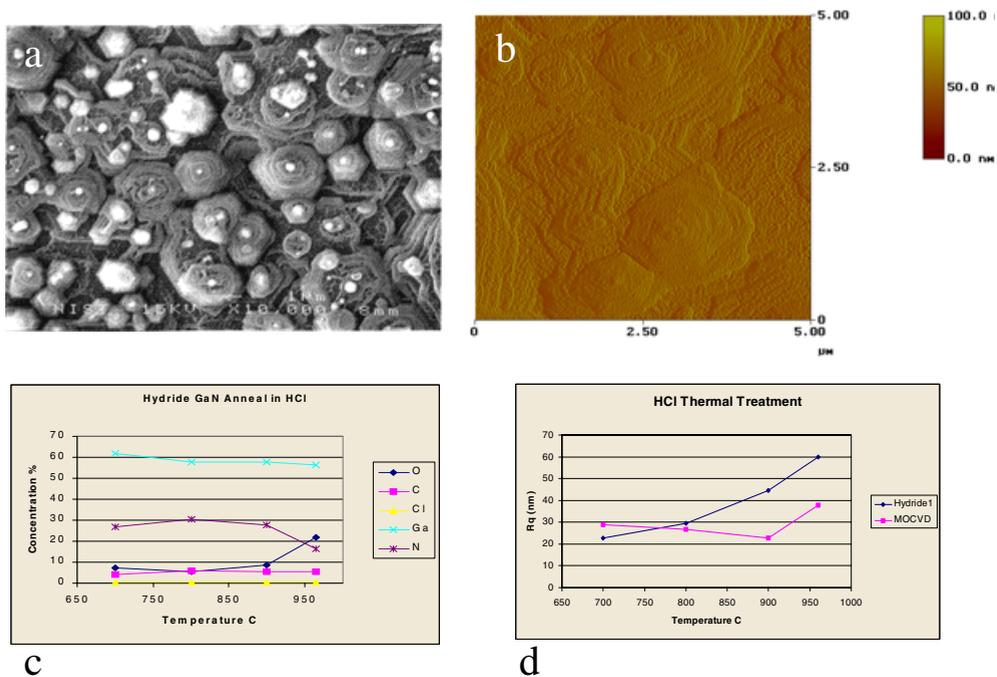


Fig. 2 (colour). HVPE GaN annealed in HCl at 965 °C; a) SEM, b) AFM, c) AES of HVPE GaN annealed in HCl; d) AFM rms roughness vs. temperature for MOCVD and HVPE GaN annealed in HCl

tion reaction for the MOCVD film can be summarized as follows:



The decomposition reaction for the HVPE GaN can be expressed as



3.3 Annealing in NH₃ The HVPE film showed a slight surface smoothing caused by a mild etching effect. It is postulated that H-containing species from decomposing NH₃ gas, may have attacked the energetically unstable island structures on the surface of the GaN. In a competing process, active nitrogen species from ammonia gas would shift the decomposition reaction: $\text{GaN}^{\text{S}} = \text{Ga}^{\text{I}} + 1/2 \text{N}_2^{\text{V}}$ to the left, thus inhibiting gallium nitride from decomposing. Overall, both MOCVD and HVPE films are relatively stable in NH₃ ambient in the temperature range studied.

3.4 Annealing in N₂ It was necessary to apply extremely high annealing temperatures for both MOCVD and HVPE GaN in order for any surface degradation to occur. HVPE films did not decompose until 1200 °C and MOCVD films were completely stable in the range studied (up to 1400 °C). Even at high temperature, minimal dependence on anneal pressure (40 to 760 Torr) was seen in the evaporation rate. A detailed study of GaN thermal behavior in vacuum, argon and nitrogen atmospheres is underway.

4. Discussion

4.1 Summary of thermal annealing This work represents a complete study of GaN annealed in HCl, H₂, NH₃ and N₂. The GaN thermal behavior was evaluated by comparison of MOCVD and HVPE samples (Table 1). In general, the MOCVD films were found to obey a dissociative sublimation mechanism while the HVPE films followed a decomposition pathway with liquid gallium droplet formation. The MOCVD films appear to have higher kinetic barrier towards decomposition. This difference cannot be accounted for by contaminants as the SIMS profile showed negligible chlorine and oxygen impurity concentrations in both films. The different polarity, and resulting crystal quality and structure account for the observed difference.

4.2 Polarity A wet etch (RT or 100 °C) with NaOH (or H₃PO₄ or H₃PO₄/H₂SO₄) rapidly etched the rough HVPE GaN surface, and in fact etched the surface into hexagonal facets. A similar result was seen with HCl gas anneals. Our wet and dry etch results agree with experimental wet etch results from [11]. Smoother MOCVD films etched slower and did not preferentially etch any of the faces of GaN. Using the prior notation, our rough HVPE films were clearly N-face, while our MOCVD films were Ga-face [12]. To understand why the N-face HVPE films were rougher, several related phenomena are easily tied together. N-face films are known to have pyramidal growth compared to Ga-face films that show a slower layer-by-layer growth mechanism. The N-face films are structurally less stable with energetic pyramidal faces that would be highly susceptible to etching. As observed in this study the N-face films etch quickly into hexagonal pyramids. A more detailed account of the thermal stability of GaN and the influence of polarity of GaN is in progress [13].

Acknowledgements The authors would like to thank Vladimir Demin, Eric Lambers, Todd Dann, and the staff at the Major Analytical Instrumentation Center and Microfabritech. This work was supported by the NSF, grant ECS-9973864 under Program Director Dr. Usha Varshney.

References

- [1] S. NAKAMURA, M. SENOH, S. NAGAHAMA, N. IWASA, T. YAMADA, T. KOZAKI, H. UMEMOTO, M. SANO, and K. CHOCHO, *Jpn. J. Appl. Phys. (Part 2)* **36**, L1568 (1997).
- [2] F. REN, C. R. ABERNATHY, J. D. MACKENZIE, B. P. GILA, S. J. PEARTON, M. HONG, M. J. SCHURMAN, A. G. BACA, and R. J. SHUL, *Solid-State Electron.* **42**, 2177 (1998).
- [3] D. D. KOLESKE, A. E. WICKENDEN, R. L. HENRY, J. C. CULBERTSON, and M. E. TWIGG, *J. Cryst. Growth* **223**, 466 (2001).
- [4] A. D. DAVYDOV and T. J. ANDERSON, *Proc. Electrochem. Soc.* **98-18**, 38 (1998).
- [5] A. PISCH and R. SCHMID-FETZER, *J. Cryst. Growth* **187**, 329 (1998).
- [6] B. V. LVOV, *Thermochim. Acta* **360**, 91 (2000).
- [7] O. M. KRYLIOUK, M. D. REED, M. A. MASTRO, T. J. ANDERSON, and B. CHAI, *phys. stat. sol. (a)* **176**, 407 (1999).
- [8] A. T. DINDSALE, *CALPHAD* **15**, 317 (1991).
- [9] I. N. PRZHEVALSKI, S. Y. KARPOV, and Y. N. MAKAROV, *MRS Internet J. Nitride Semicond.* **3**, 1 (1998).
- [10] B. SUNDMAN, B. JANSSON, and J. O. ANDERSSON, *CALPHAD* **9**, 153 (1985).
- [11] J. L. WEYHER, S. MULLER, I. GRZEGORY, and S. POROWSKI, *J. Cryst. Growth* **182**, 17 (1997).
- [12] E. S. HELLMAN, *MRS Internet J. Nitride Semicond.* **3**, 11 (1998).
- [13] M. A. MASTRO, O. M. KRYLIOUK, M. D. REED, T. J. ANDERSON, A. DAVYDOV, and A. SHAPIRO, *J. Cryst. Growth*, to be published.

