



Influence of polarity on GaN thermal stability

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Abstract

A comparative study of the stability of Ga- and N-polar GaN films was made in different gas ambients (N_2 , H_2 , NH_3 , HCl). The Ga-polar films were observed to undergo a dissociative sublimation, while the N-polar films formed condensed Ga in addition to the gaseous species. The difference in polarity affects the morphology and bonding on the surface, and thus, stability of the atoms bonded to the surface.

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1. Introduction

Thermal decomposition of solids is of practical interest because of its fundamental presence in the fabrication, application and degradation of solid-state materials. Although factors such as heat input, chemical reaction and gas-phase mass transport exist at each stage of thermal decomposition, typically the evaporation step is the

controlling mechanism. Volatilization is composed of three primary steps: (1) the transfer of thermal energy into the solid, (2) surface processes leading to formation of vapor molecules, (3) transport of vapor away from the surface [1].

The recent developments of GaN-based blue light-emitting diodes (LEDs) and lasers [2] and high-power/high-temperature electronics [3] have produced an intense interest in the column III-nitrides. The thermal and chemical stability of GaN and related materials are important to growth and device processing, and is not well understood. As examples, the mechanisms of growth and the role of post-growth annealing in defect reduction are related to thermal stability as

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well as differences in implant activation pathways (Si, Mg) and the interfacial reactions between GaN and metal contacts. A detailed study of the stability of GaN in various ambients is important to the understanding of these issues as well as the future development of complex devices.

On heating, GaN can undergo the following possible routes depending on the annealing conditions (Fig. 1): etching (dissociative and congruent sublimation) or incongruent decomposition accompanied by nitrogen-saturated liquid Ga droplet formation [4–10]. A series of decomposition

experiments were performed that revealed the decomposition or etching of GaN depending on the nature of the ambient gas, annealing temperature, and polarity.

This group previously reported a comparative thermal stability study of MOVPE versus HVPE GaN films [11]. The observed difference in stability is accounted for by the difference in polarity of films and not the particular growth technique. This difference in polarity affects the bonding on the surface (reconstruction) and thus stability of the atoms bonded to the surface.

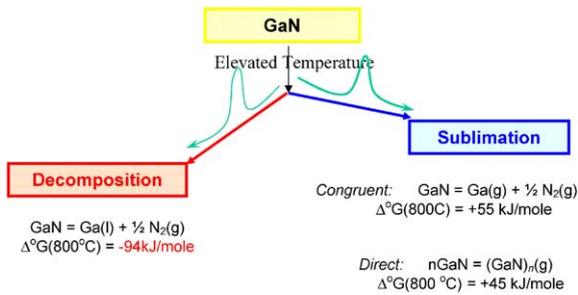


Fig. 1. Kinetic effects can be important, as highly activated barriers can exist causing thermal behavior to be non-equilibrium.

2. Experimental Procedure

The details of growth were described in Ref. [11]. Henceforth, the annealed samples will be referred to only by their polarity and not the particular growth technique for clarity.

A summary of the experimental annealing conditions is given in Table 1a. The samples used in this study were loaded as-grown, that is, the samples received no additional cleaning. The furnace was pre-heated to the particular annealing temperature. The load–lock system allowed sam-

Table 1

(a) Annealing Conditions of Ga- and N-polar GaN Samples

Conditions	Ga- and N-polar GaN
Conditions	HCl; 760 Torr H ₂ ; 760 Torr NH ₃ ; 760 Torr N ₂ ; 760 Torr and 76 Torr
Time	30 min
Temperature	500–1400 °C

(b) GaN thermal behavior comparison of Ga- and N-polar samples

Annealing gas	Polarity	Mechanism	Evaporation point (°C)	Comment
HCl	Ga-polar	Sublimation	800	Slight Etching above 800 °C
	N-polar	Decomposition	800	Etching above 900 °C
H ₂	Ga-polar	Sublimation	800	Completely sublimed by 900 °C
	N-polar	Decomposition	800	100 μm droplets at 900 °C
NH ₃	Ga-polar	Sublimation	Small effect at 965	Roughens Above 800 °C
	N-polar	Decomposition	Small effect at 965	Smooths above 800 °C
N ₂	Ga-polar	Negligible	Completely stable to 1400	From 40–760 Torr
	N-polar	Decomposition	1200	Negligible influence from pressure

ples to be loaded into the hot furnace. The load-lock system also allowed multiple pump/purge cycles to prevent contaminating the system with oxygen. The sample was loaded with a magnetic arm and after allowing approximately 5 min for the temperature in the furnace to stabilize, the anneal gas was sent to the system for 30 min. The system was flushed with nitrogen for 5 min after the experiment was completed to remove any hazardous gases. The sample was then unloaded and the new temperature was set.

3. Results

This section reports on a study of GaN decomposition in H_2 , HCl, NH_3 and N_2 (the most common processing gases). The differences between Ga- and N-polar films in these gases were

compared. All films were characterized by use of atomic force microscopy (AFM) and scanning electron microscopy (SEM) for surface structure, and auger electron Spectroscopy (AES), SEM, and EDS for chemical composition.

3.1. Annealing in H_2

3.1.1. Anneal of Ga-polar GaN

For Ga-polar GaN films annealed in H_2 up to $700^\circ C$, no change in film composition or morphology is observed. AES (Fig. 2a) shows that at $900^\circ C$, Ga and N concentrations are dramatically reduced thus Ga and N have left the surface as a gas, resulting in a GaN surface that is almost entirely sublimated.

SEM of Ga-polar GaN annealed in H_2 at $800^\circ C$ (Fig. 2b) shows partial sublimation of GaN (white areas = GaN) with no Ga droplets observable by EDS. SEM of $900^\circ C$ in H_2 anneal (Fig. 2c) agrees

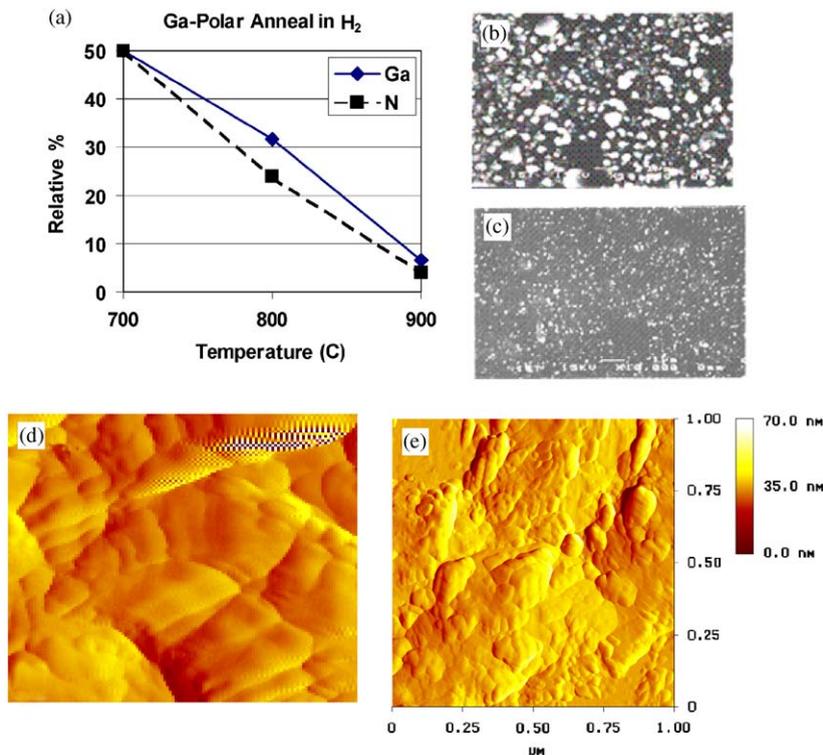
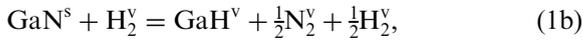


Fig. 2. Ga-polar GaN annealed in H_2 (a) AES; SEM at: (b) $800^\circ C$, (c) $900^\circ C$; AFM at: (d) $700^\circ C$, (e) $900^\circ C$.

with AES analysis as GaN is nearly completely sublimed with only the substrate (black area) remaining. Fig. 2d and 2e, shows that the surface morphology worsens as the GaN sublimation rate increases with anneal temperature. At 900 °C only the substrate remains. The sublimation reaction for the Ga-polar film can be summarized by three independent reactions:



3.1.2. Anneal of N-polar GaN

Fig. 3b shows that the decomposition of N-polar GaN annealed in H₂ starts at 800 °C, evident by the small-size Ga droplets (white areas) forming at defects in the film (Fig. 3d). SEM contrast allows the island growth and dislocation defects to be discernible (Fig. 3c). As evident in the SEM micrograph displayed in Fig. 3e, N-polar GaN decomposition is accompanied by the formation of large Ga droplets (~100 μm) on the surface. This is also evident in the AES spectrum in Fig. 3a, which shows nitrogen loss while the Ga concentration remains constant.

From Fig. 3f and g, it is seen that the N-polar films roughen as they decompose. The onset of

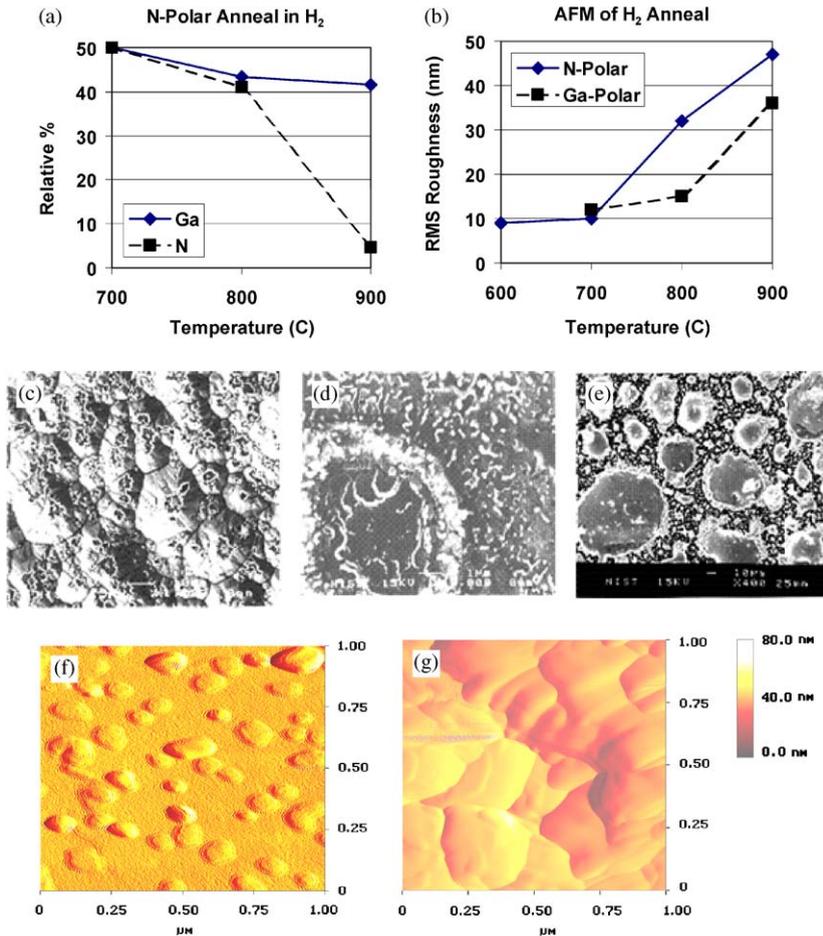
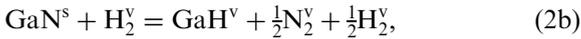


Fig. 3. GaN annealed in H₂ (a) AES of N-polar GaN; (b) AFM RMS roughness vs. temperature for Ga- and N-polar GaN; SEM of N-polar at (c) 800 °C, (d) 900 °C, (e) 960 °C; AFM of N-polar at: (f) 800 °C, (g) 960 °C.

sublimation for Ga-polar films (above 800 °C) is approximately 100° less than decomposition of N-polar films (above 700 °C). The decomposition reaction of GaN in hydrogen can be expressed as these three independent reactions:

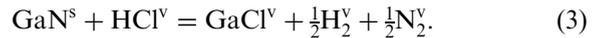


3.2. Annealing in HCl

3.2.1. Anneal of Ga-polar GaN

A comparison of Ga-polar GaN for different anneal temperatures was performed under HCl gas. As is evident from the series of SEM pictures in Fig. 4a–c the surface of the GaN is still intact at 800 °C. At 900 °C, these films begin to show a sublimation mechanism. EDS analysis revealed that at higher temperatures Ga and N leave the surface simultaneously as a gas, indicative of a

congruent sublimation mechanism. This is seen in Fig. 4a–c, where the white area is GaN, the gray is the original GaN, and the black is the sapphire substrate. At 900 °C, nearly $\frac{1}{4}$ of the film has sublimated leaving only the substrate (black areas). By 965 °C, approximately $\frac{3}{4}$ of the film has sublimated. The surface of the Ga-polar films has excellent structural quality and specular surfaces. Fig. 4d shows AES of Ga-polar 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 Ga-polar GaN follow a dissociative sublimation route that can be expressed as the following simplified reaction:



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 [4,5] and for all possible gas species in the Ga–N–H–Cl system [12,13] employing Thermo–Calc software [14].

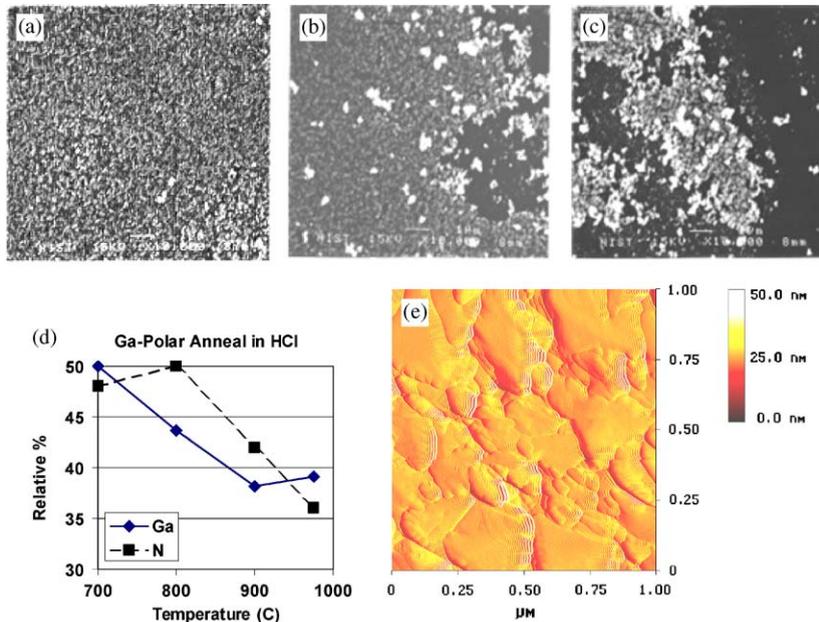
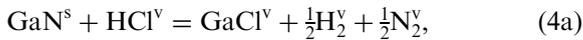


Fig. 4. Ga-polar GaN annealed in HCl; SEM at: (a) 800 °C, (b) 900 °C, (c) 965 °C; (d) AES of Ga-polar GaN annealed in HCl; (e) AFM of Ga-polar annealed in HCl at 900 °C.

3.2.2. Anneal of N-polar GaN

Fig. 5a shows Ga droplets on top of GaN hexagonals. Nitrogen desorbs from the surface, leaving Ga liquid droplets on the surface that solidify upon cooling. Thus, at high temperature, partial decomposition occurs for N-polar films under HCl gas. In Fig. 5b, hexagonal pyramids similar to those in Fig. 5a are observable. In Fig. 5c, AES shows decomposition of the GaN (by a decrease in only nitrogen concentration) at higher temperatures.

A plot of AFM RMS roughness as a function of anneal temperature shows the difference between Ga- and N-polar films (Fig. 5d). Ga-polar films begin to roughen above 900 °C as the sublimation mechanism takes over. Fig. 5d shows that the N-polar films begin to roughen at 800 °C. The reaction of N-polar GaN film with the HCl gas can be expressed by two independent reactions:



3.3. Annealing in NH₃

3.3.1. Anneal of Ga-polar GaN

In Fig. 6d, AES shows the Ga and N concentrations are constant thus, no sublimation of the Ga-polar GaN film annealed in NH₃ has occurred. AFM pictures of Ga-polar films (Fig. 6a–c) reveal that a mild etching mechanism occurs. There is no significant change in roughness with anneal temperature (Fig. 6e) for either Ga-polar or N-polar films.

3.3.2. Anneal of N-polar GaN

For the N-polar GaN annealed in NH₃ a slight surface smoothing caused by a mild etching mechanism is observed. It is postulated that H decomposes from NH₃ to attack the energetically unstable island structures on the surface of the GaN. No compositional change of N-polar films by AES analysis is observed. Overall, both Ga- and N-polar films are relatively stable in

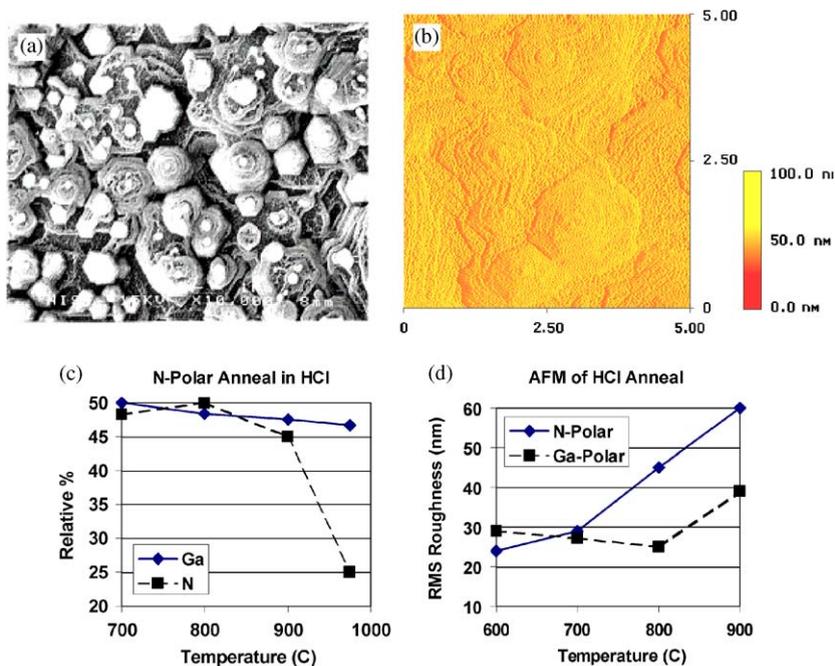


Fig. 5. N-polar GaN annealed in HCl at 965 °C: (a) SEM, (b) AFM; (c) AES of N-polar GaN annealed in HCl; (d) AFM RMS roughness vs. temperature for Ga- and N-polar GaN annealed in HCl.

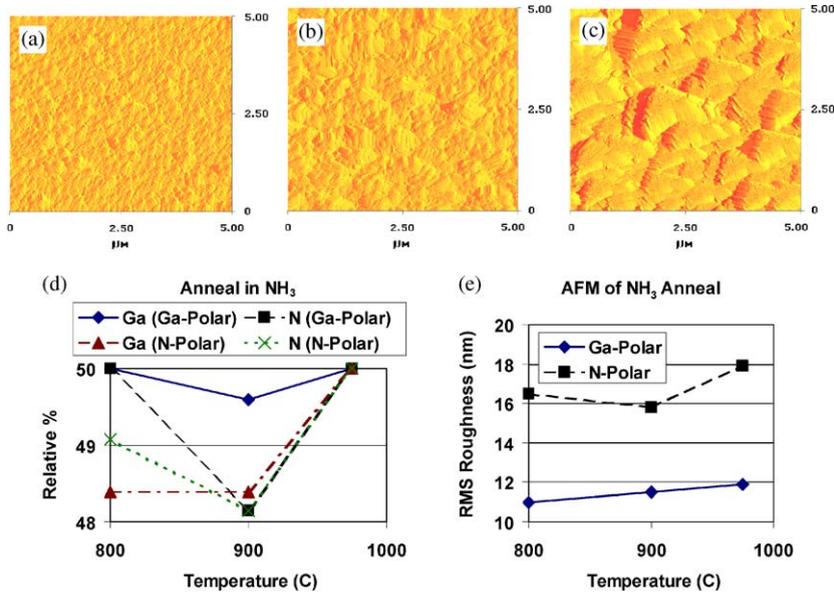


Fig. 6. GaN annealed in NH₃; AFM of Ga-polar at (a) 800 °C, (b) 900 °C, (c) 965 °C; (d) AES of Ga-polar; (e) AES of N-polar; (f) RMS roughness of Ga- and N-polar.

NH₃ ambient in the temperature range studied (Fig. 6d,e).

In a competing process, active nitrogen species from ammonia gas would shift the decomposition reaction: $\text{GaN}^{\text{s}} = \text{Ga}^{\text{l}} + \frac{1}{2}\text{N}_2^{\text{v}}$ to the left, thus inhibiting GaN from decomposing. Therefore, at the above conditions, the reaction of both Ga- and N-polar GaN with ammonia is insignificant and is hindered by the kinetic stability of NH₃ species.

3.4. Annealing in N₂

Ga-polar GaN films are very stable during a N₂ anneal. It was necessary to apply extremely high anneal temperatures for both Ga- and N-polar GaN in order for any surface degradation to occur. N-polar films did not decompose until 1200 °C and Ga-polar films were completely stable in the range studied (up to 1400 °C). Even at high temperature, minimal dependence on anneal pressure (760–40 Torr) was seen in the evaporation rate.

4. Discussion

4.1. Summary of thermal annealing and the influence of polarity

This work represents a complete study of Ga- and N-polar GaN annealed in HCl, H₂, NH₃ and N₂. The GaN thermal behavior was evaluated by comparison of Ga- and N-polar samples. A summary of the results is presented in Table 1b. In general, the Ga-polar films were found to obey a dissociative sublimation mechanism while the N-polar films followed a decomposition pathway with liquid gallium droplet formation. This difference cannot be accounted for by contaminants as a SIMS profile and AES showed negligible chlorine and oxygen impurity concentrations in both films. It is known that GaN films can be grown by MOVPE and HVPE (as well as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD)) either N- or Ga-polarity depending on the growth conditions, particularly the initial stages of growth. This variation in polarity (not the particular growth technique) and resulting crystal

structure accounts for the observed difference in thermal stability.

Thermodynamic calculations above predicted two possible reaction mechanisms to occur on the surface of GaN during exposure to elevated temperature. The particular vaporization mechanism is determined by surface kinetics that vary according to the polarization of the film and thus the adlayer and bulk bonding arrangement.

In this report, initial vaporization temperature points were reported for Ga- and N-polar films under four different processing gases. Presumably, vaporization begins at a slightly lower temperature that is undetectable by SEM (with EDS), AFM, AES, or optical microscopy. Mayumi et al. [15] studied the decomposition of Ga- and N-polar GaN in hydrogen by in-situ gravimetric monitoring. Mayumi found that both Ga- and N-polar GaN films had a transition temperature of 820–850 °C between a slow vaporization rate ($r = Kp^{1/2}H_2$) and a rapid vaporization rate ($r = kP^{3/2}H_2$), where r and k are the decomposition rates and rate constants, respectively [15]. In this paper, the experimental vaporization points correspond to this transition temperature. It was found experimentally that under H_2 or HCl ambient, both polarities of GaN displayed vaporization above 800 °C. It is not surprising that the HCl anneal resulted in a similar vaporization temperature as the H_2 anneal in this study and in the work by Mayumi, as HCl decomposes into active H at elevated temperature. Mayumi observed more rapid vaporization rates for N-polar GaN compared to Ga-polar GaN at elevated temperature. This was attributed to the difference in Ga adlayer bonding configuration to the surface atoms of N- and Ga-polar GaN crystal.

4.1.1. N-polar

For N-polar GaN at elevated temperature, it was observed by Shen et al. [16] that N atoms leave the surface while excess Ga atoms are incorporated at the surface with only a small fraction of the Ga atoms evaporating from the surface. Tsai et al. [17] showed that for the bonding arrangement of a Ga-adlayer on N-polar GaN, it is favorable for the Ga atoms to remain on the surface [17].

Tsai used first-principle calculations to verify that Ga adatoms bind favorably to the N-polar of GaN. The Ga adatoms coordinate with three other Ga adatoms and one N surface atom for a total of four bonds. This is a stable structure with no dangling bonds present [17].

In N-polar films, two mechanisms further enhance the decomposition rate. It is well known that N-polarity films show small grain features while Ga-polarity films are smooth and uniform. Grain boundary areas contain high density of dislocations that are considered unstable [16]. Stach et al. [18] showed by in situ transmission electron microscopy that nitrogen rapidly desorbed along dislocation cores. In this paper, this decomposition enhancement mechanism at dislocations was experimentally seen in Fig. 3c–e.

Additionally, once Ga^1 forms on the surface, a catalytic enhancement is predicted to occur. An alternate pathway with lower activation energy is provided when a surface liquid is used to dissolve GaN, acting as a catalyst. The liquid disrupts the rigid crystal structure during the solution process. The nitrogen atoms are then free to migrate into the liquid to form N_2 molecules that can diffuse through the liquid and escape to the liquid–gas interface, where vaporization occurs [19]. Conceivably, any liquid metal with a certain solubility of GaN can change the defect concentration at the surface of the crystal lattice, thus influencing the evaporation rate. The Ga atoms precipitate out in the form of a liquid at the surface due to their low vapor pressure while the nitrogen atoms associate and subsequently diffuse through the liquid metal [19].

Schoonmaker et al. [20] found that the decomposition of pure GaN in nitrogen was too small to measure, however, when liquid gallium or indium was placed on the surface, the rate was greatly enhanced [21]. The enthalpy of evaporation for $Ga^1 \rightarrow Ga^v$ is 256 KJ/mol which results in a bulk $Ga^1 \rightarrow Ga^v$ vaporization rate that is much slower than the GaN decomposition rate thus, allowing the accumulation of Ga on the surface [22]. In this investigation, Ga^1 droplet formation was clearly seen for a number of annealed N-polar GaN samples (e.g., Figs. 3d,e; 5a).

4.1.2. Ga-polar

For Ga-polar materials, Ga adatoms are weakly bonded to the Ga atoms on the surface of the GaN crystal. The Ga–Ga bond is weaker than the Ga–N bond (2.17 eV) [16,23–25]. At elevated temperature, the Ga atoms of the Ga adatom layer possess a low barrier for evaporation from the surface [16].

Similarly, Tsai et al. [17] calculated for a Ga-polar GaN surface that the Ga- and N-layer separation in the two top bi-layers is 0.115 and 0.083, respectively. This is larger than the bulk bi-layer separation of 0.077 nm thus, the surface is relaxed outwards. This leads to a decrease in the work function at the surface, which predicts that the Ga adlayer formed on the surface will be unstable [17]. Therefore, it cannot be predicted that Ga atoms will accumulate on the surface, and this prevents the catalytic enhancement of the vaporization rate phenomena. Furthermore, the planar, uniform surface of the Ga-polar GaN does not possess large grain boundaries that would act as sites for enhanced vaporization [16].

5. Conclusion

Using our annealing study we were able to study the GaN surface after exposure to several ambient gases by AFM, AES, SEM, and EDS. Theoretical descriptions of the surfaces of Ga- and N-polar GaN were introduced to explain how film polarity influences the vaporization of N- and Ga-polar GaN. The experimental results correlated with the theoretical predictions which indicate the mechanism that GaN films would follow when exposed to elevated temperatures.

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