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## THERMAL ANNEAL EFFECTS ON CARBON-HYDROGEN LVMs IN AlGaN

M. O. Manasreh\*, and B.D. Weaver\*\*

\*Department of Electrical and Computer Engineering, University of New Mexico,  
Albuquerque, New Mexico 87131

\*\*Naval Research Lab, 4555 Overlook Ave, SW, Washington, DC 20375

### ABSTRACT

Thermal annealing effects on carbon-hydrogen (C-H) complexes defects in AlGaN grown on sapphire by metalorganic chemical vapor deposition (MOCVD) technique have been investigated using Fourier transform infrared spectroscopy (FTIR). The CH complexes in AlGaN, formed either during growth or by proton irradiation, exhibit five local vibrational modes (LVMs) due to the symmetric and asymmetric vibrational stretching modes of C-H in  $\text{CH}_n$  ( $n=1-3$ ) defect complexes. It was found that the annealing temperature ( $T_a$ ) of  $500^\circ\text{C}$  is sufficient enough to dissociate most of the C-H complexes in AlGaN samples. A turning point annealing temperature is found around  $300^\circ\text{C}$  for un-irradiated Mg-doped sample, below which the total integrated area of the C-H LVMs continued to increase with increasing annealing temperature and reach the maximum value around  $300^\circ\text{C}$ . At  $T_a > 300^\circ\text{C}$ , the total integrated area of the C-H LVMs starts to decrease and the C-H complexes seem to be completely depleted at  $T_a > 600^\circ\text{C}$ . The depleted C-H LVMs were observed to partially recover after thermal annealing at  $T_a > 500^\circ\text{C}$  and waiting for aging periods of several days. This recovery behavior is explained in terms of the hydrogen being remained inside the crystal after the dissociation of C-H complexes, subsequent diffusion and recombining again with carbon atom to reform C-H complexes.

### INTRODUCTION

Optoelectronic devices based on III-nitrides and their ternary alloys have a broad range of application due to their wide direct band-gaps covering the spectral range from visible to ultraviolet. GaN has unique applications in blue, green and ultraviolet-blue light-emitting diodes, detectors and laser diodes [1-4]. III-nitride material system also shows tremendous potential in the field of high-temperature and high-power electronics because of their superior materials parameters [5]. Omnipresent impurities such as carbon, hydrogen and oxygen play detrimental and beneficial roles in fabrication processes. For example, hydrogen can passivate the acceptor Mg [6-8] in GaN. Hydrogen can be easily incorporated into III-nitride during or after the growth of the materials [8]. Ion irradiation represents a very attractive tool for several technological steps, such as electrical and optical selective-area doping, dry etching and electrical isolation, in III-nitride based devices' fabrication. Compare to the understanding of ion beam process in mature semiconductors (i.e. Si and GaAs), the understanding of the complex ion beam process in III-nitrides is still at its infancy. Therefore, understanding of thermal annealing behavior of complexes defects will help the understanding of dopant incorporation and application of ion implantation.

In this paper, we report on some results of thermal annealing behavior of C-H complexes defects formed unintentionally or by proton irradiation in AlGaN. The evolutions of C-H LVMs

in proton irradiated sample as a function of thermal annealing and the aging effect of the sample annealed at  $T_a > 500^\circ\text{C}$  are presented.

## EXPERIMENT DETAILS

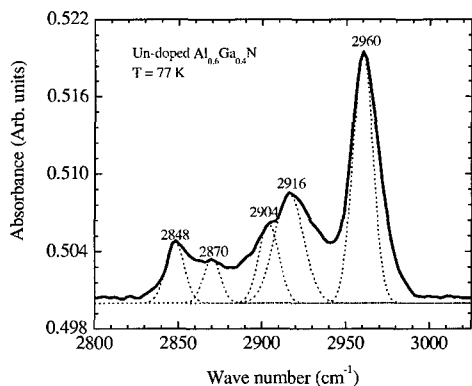
Furnace rapid thermal annealing was performed on three samples to investigate the thermal annealing behavior of C-H complexes in as-grown and proton irradiated AlGaN. All the samples used in this study were grown on sapphire substrate with AlN buffer layer using the MOCVD technique. The infrared (IR) absorption measurements were performed with a BOMEM Fourier-transform spectrometer (FTIR), which covers the spectral range of 450-4500  $\text{cm}^{-1}$ . A KBr beamsplitter, a globar light source, and a liquid-helium-cooled Si-B detector in conjunction with a continuous flow cryostat were used. A special sample holder was constructed to let the incident light from the spectrometer reach the sample at the Brewster's angle. This configuration proved to be very useful to avoid the interference patterns generated from the substrate as well as from the epitaxial thin film. The temperature was controlled within  $\pm 1.0\text{K}$  and the spectra were measured at both 300 K and 77 K.

The three samples are undoped  $\text{Al}_{0.6}\text{Ga}_{0.4}\text{N}$  sample [denoted as (A)], Si-doped  $\text{Al}_{0.6}\text{Ga}_{0.4}\text{N}$  sample [denoted as (B)] and Mg-doped  $\text{Al}_{0.4}\text{Ga}_{0.6}\text{N}$  sample [denoted as (C)]. Sample A was irradiated with 1MeV proton and doses  $5.0 \times 10^{16} \text{cm}^{-2}$ . All these samples were sandwiched between two boron nitride wafers to reduce the loss of nitride and ionization and heated in a continuous flow of  $\text{N}_2$ . For Mg-doped  $\text{Al}_{0.4}\text{Ga}_{0.6}\text{N}$  sample, [sample (C)], it was heated at a sequence of temperatures from 100 to  $900^\circ\text{C}$  in steps of  $50^\circ\text{C}$ , and the annealing time was 2 minutes at  $T_a \leq 700^\circ\text{C}$  and 15 minutes at  $T_a \geq 750^\circ\text{C}$ . IR absorbance measurements were made just after each annealing treatment on sample (C) as well as after waiting for periods of several days for each annealing treatment. This procedure allows us to observe the variation of the C-H LVM intensities and the aging effect. The aging effect was performed at each annealing temperature above  $500^\circ\text{C}$ .

## EXPERIMENTAL RESULTS

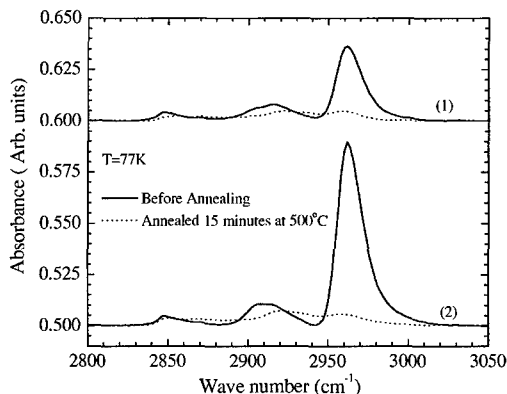
All the samples tested in this study were found to contain five IR peaks in the spectral range of  $2846 - 2963 \text{cm}^{-1}$ . Figure 1 shows FTIR spectrum for undoped  $\text{Al}_{0.6}\text{Ga}_{0.4}\text{N}$  sample implanted with 1MeV proton and a dose of  $1 \times 10^{16} \text{cm}^{-2}$ . This spectrum can be resolved into five peaks at 2849, 2870, 2902, 2918 and  $2960 \text{cm}^{-1}$ . Based on a comparison with the LVMs measurement in GaN and calculated C-H frequencies in  $\alpha\text{-Si}_{1-x}\text{C}_x\text{H}$  [9-12], we ascribe these five peaks to symmetric and asymmetric stretching modes of  $\text{CH}_n$  ( $n=1,2,3$ ) complexes in AlGaN. The absorption peak at  $2848 \text{cm}^{-1}$  is attributed to a stretching mode of CH; the peaks at  $2904$  and  $2916 \text{cm}^{-1}$  are attributed to a symmetric and an asymmetric stretching mode of  $\text{CH}_2$ , respectively; and the peaks at  $2870$  and  $2960 \text{cm}^{-1}$  are attributed to symmetric and asymmetric stretching mode of  $\text{CH}_3$ .

Figure 2 shows IR absorbance spectra of sample (A) (spectrum 1) and sample (B) (spectrum 2) measured before (solid line) and after 15 minutes (dotted line) thermal annealing at  $500^\circ\text{C}$ . Thermal annealing behavior of LVMs spectra of C-H complexes in sample (C) is shown in Fig. 3 (a), (b) and (c). Fig. 3(a) shows the LVMs spectral behavior as the annealing temperature is changed. Fig. 3(b) shows spectra for the same sample annealed at higher temperatures. These spectra were measured just after thermal annealing (dotted spectra) and

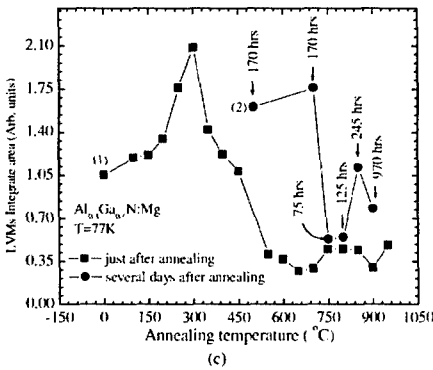
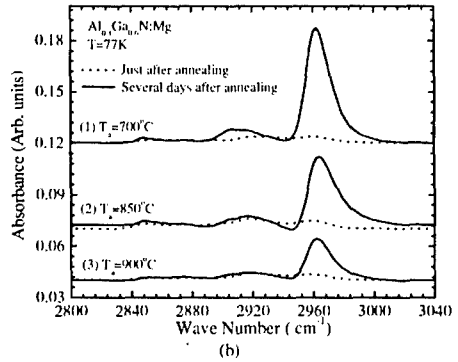
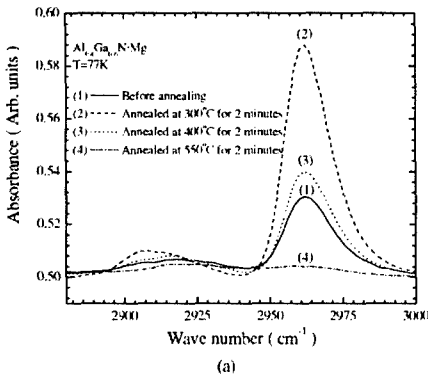


**Figure 1.** Infrared absorption spectrum measured at 77K for a proton irradiated  $Al_{0.6}Ga_{0.4}N$  sample. The IR absorption peaks are resolved into five peaks at 2848, 2870, 2904, 2916 and 2960  $cm^{-1}$ . The solid line is the actual spectrum while the dotted lines are Gaussians added to the spectrum for clarification.

several days after thermal annealing was performed (solid spectra). The data labeled (1) in Fig. 3 (c) show the total integrated areas of CH LVMs in sample (C) tested just after each annealing treatment. While the data for the integrated areas labeled (2) in this figure were obtained after annealing the samples and waiting for periods of 170 hours or higher as indicated in the figure. The data labeled (1) in Fig. 3(c) clearly show an increase in the total integrated area as the annealing temperature is increased from 0 to 300°C. As  $T_a$  is increased above 300°C, the integrated area starts to decrease and essentially vanished at  $T_a$  above 600°C. But then the CH LVMs seem to recover after waiting for a period of 170 hours or higher as indicated in the data labeled (2). The LVMs spectra of sample (C) in Fig. 3(b) were obtained just after each annealing (dotted spectra) and after waiting for a period of several days (solid spectra) at  $T_a = 700$  (spectra 1), 800 (spectra 2) and 900°C (spectra 3). It is obvious that a partial recovery of CH LVMs occurs when the samples were tested one week after thermal annealing. It is also noted that the general trend is that the total integrated areas of the C-H LVMs is decrease as the annealing temperature is increased above 300°C for both before and after the aging [see Fig. 3(c)].



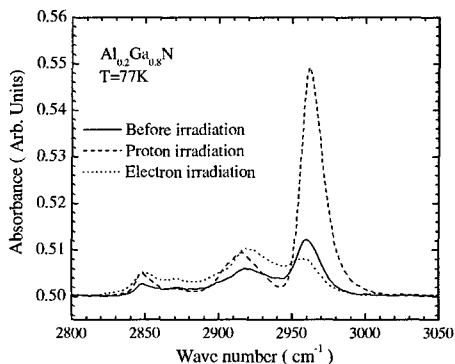
**Figure 2.** LVMs spectra measured before annealing (solid line) and after 15 minutes annealing at 500°C (dot line) in sample (1), (2) are shown. Sample (1) is Si-doped as-grown  $Al_{0.6}Ga_{0.4}N$ . Sample (2) is un-doped  $Al_{0.6}Ga_{0.4}N$  with 1MeV proton irradiation at the dose of  $5 \times 10^{16} cm^{-2}$ . All the measurements were carried out at 77K.



**Figure 3.** (a) LVMs spectra of CH complexes measured at 77K in Mg-doped  $Al_{0.4}Ga_{0.6}N$  sample measured after thermal annealing at  $T_a=300, 400,$  and  $550^\circ C$ . (b) The same as (a) but  $T_a=700, 850,$  and  $900^\circ C$ . The dotted lines represents the spectra measured just after thermal annealing while the solid lines represent the spectra measured several days after thermal annealing. (c) Total integrated areas of C-H LVMs measured for the Mg-doped  $Al_{0.4}Ga_{0.6}N$  sample. Data labeled (1) were obtained after thermal annealing and data labeled (2) were obtained several days after thermal annealing. The number of hours in the graph represents the waiting periods used to measure the spectra after thermal annealing.

## DISCUSSIONS

To illustrate that the observed LVMs are due to C-H complexes, we cut two pieces from an  $Al_{0.2}Ga_{0.8}N$  wafer and one piece was irradiated with 1 MeV protons and the other was irradiated with 1MeV electrons (dose =  $1 \times 10^{17} cm^{-2}$ ). The results are shown in Fig. 4. The solid line is the spectrum obtained from the samples before irradiation, the dashed line is the spectrum obtained for the proton irradiated sample, and the dotted line is the spectrum obtained from the electron irradiated sample. It is clear that proton irradiation increases the formation of C-H complexes as judged by the large increase in the stretching mode frequency of the  $CH_3$  complex. An increase of the stretching mode frequencies for  $CH_2$  and  $CH$  is also observed. However, the electron irradiated sample shows a noticeable decrease in the  $CH_3$  stretching mode. This clearly demonstrates that electron irradiation break up the  $CH_3$  complex in good agreement with others [13,14]. There is an increase of the  $CH_2$  and  $CH$  concentrations in the electron irradiated sample as seen from the increase in the area under the LVMs stretching modes. This is most likely due to the fact that  $CH_3$  is decomposed into C, H, CH, and  $CH_2$ . This behavior is observed in several samples. Additionally, Hall effect measurements show a slight increase in the carrier concentration in the electron irradiation samples. This does not seem to be universal since a



**Figure 4.** Local vibrational modes spectra measured for two samples cut from the same  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$  wafer. The solid line is the spectrum obtained for both samples before irradiation, the dashed line represents the spectrum obtained for the proton irradiated sample (dose= $6 \times 10^{16} \text{cm}^{-2}$ ), and the dotted line represent the spectrum obtained for the electron irradiated (dose= $1 \times 10^{17} \text{cm}^{-2}$ ) sample.

few samples show a slight decrease in the carrier concentration after electron irradiation. Figure 3 (a) and (b) show the thermal annealing effect on C-H LVMs. The asymmetrical stretching mode of  $\text{CH}_3$  is affected dramatically by thermal annealing as compared to other stretching modes of  $\text{CH}_2$  and  $\text{CH}$ . This means that  $\text{CH}_3$  is thermally unstable. It is observed from Fig. 3 (c) that the LVMs integrated area of C-H complexes in Mg-doped sample is increased with increasing annealing temperature and it reaches a maximum value after annealing the sample at  $300^\circ\text{C}$ . This proves that C-H complexes in AlGaIn are stable below  $300^\circ\text{C}$ . Thermal annealing at  $T_a < 300^\circ\text{C}$  seems to help the formation of C-H. The C-H LVM intensities decrease after thermal annealing treatment at  $T_a > 300^\circ\text{C}$  due to the dissociation of C-H complexes. After the thermal dissociation of C-H complexes, H either lose an electron and becomes  $\text{H}^+$ , which could have a higher probability of recombining with  $\text{C}^-$  and reforming the passivated complexes, or it captures a second electron to form  $\text{H}^-$ . This of course will not recombine with  $\text{C}^-$ , and it is likely to migrate further away due to Coulomb repulsion and could eventually form either a molecule by combining with an  $\text{H}^+$  or a larger H cluster or aggregate. C-H complexes seem to be completely depleted at  $T_a > 600^\circ\text{C}$ .

## CONCLUSION

We presented the local vibrational modes spectra of C-H complexes in annealed AlGaIn grown by MOCVD technique. Thermal annealing at temperature around  $500^\circ\text{C}$  is sufficient enough to dissociate most of the C-H complexes in AlGaIn thin film. However, a partial recovery of the CH LVMs is observed in thermally annealed samples at  $T_a > 500^\circ\text{C}$ . This intriguing behavior is explained in terms of C-H recombination, which strongly suggests that H atoms remain trapped in the sample even after C-H decomposition. However, the integrated areas of the C-H LVMs are decreased after thermal annealing and aging as the annealing temperature is increased. While proton irradiation cause a drastic increase in the  $\text{CH}_3$  LVM, electron irradiation cause the opposite effect suggesting strongly that the observed LVMs are truly due to CH complexes.

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