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Gamma-ray irradiation effects on Fourier transform infrared grazing incidence reflection–absorption spectra of GaN films

W H Sun¹, J C Zhang¹, L Dai^{1,2}, K M Chen¹ and G G Qin^{1,3,4}

¹ Department of Physics, Peking University, Beijing 100871, People's Republic of China

² Mesoscopic Physics Laboratory, Peking University, Beijing 100871, People's Republic of China

³ International Center for Materials Physics, Academia Sinica, Shenyang 110015, People's Republic of China

E-mail: qingg@pku.edu.cn

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Abstract

We have studied the effects of gamma-ray irradiation on the Fourier transform infrared grazing incidence reflection–absorption spectra of GaN films grown on α -Al₂O₃ (0001) substrates using metal-organic chemical vapour deposition at atmospheric pressure. After irradiation, the spectral intensity increased markedly and a series of new absorption features appeared, among which those at 3440, 3355, 3174, 3088, 2819, 2712, 2100, 1426 and 894 cm⁻¹ are discussed and identified. The reason why gamma-ray irradiation can enhance the intensity and give rise to these new features is also discussed.

1. Introduction

During the past several years, GaN has been established as a basic material for ultraviolet-blue light emitting diodes and laser diodes [1]. Although basic research on GaN has been going on for nearly three decades, many fundamental physical problems remain unresolved [2]. Infrared (IR) absorption spectroscopy is a useful and effective tool for studying the lattice vibration of semiconductors and features of light impurities, such as H, C and O in semiconductors [3–5]. H-, C- and N-related complexes in GaN have been studied employing IR transmission measurements [6–8], but three problems occur commonly in these measurements. (1) In most cases, the signals of the local vibration modes (LVMs) of light-impurity-related complexes in GaN films are too weak to be measured because the thickness of the films is usually only several microns. (2) The IR transmission signals are often concealed by those from the substrates on which the films were grown. For example, we cannot detect the IR-active vibrations below 1200 cm⁻¹ in GaN films grown on α -Al₂O₃ substrates due to the high absorption of the substrate in this wavenumber range. (3) IR transmission measurement is only sensitive with regard to the absorption component for the dipole moment parallel to the sample surface. However, the

⁴ Corresponding author.

Fourier transform infrared grazing incidence reflection–absorption (FTIR-GIRA) method can resolve these three problems quite well [9]. As far as we know, although there are FTIR-GIRA studies on molecules and radicals adsorbed on metals in the literature [10, 11], few such studies have been reported for GaN [9]. Here we report for the first time that gamma-ray irradiation can give rise to new features in the FTIR-GIRA spectra of GaN, and discuss its mechanisms.

2. Experiment

In the growth process of GaN for fabricating optoelectrical devices, Zn impurities are often incorporated in the epilayers as luminescence centres to enhance the blue-light luminescence intensity [12]. In this study, GaN films with light Zn doping were grown by the conventional two-flow atmospheric pressure metal-organic chemical vapour deposition (MOCVD) process, with trimethylgallium (TMG), ammonia (NH₃) and diethylzinc (DEZn) used as reactants and hydrogen and nitrogen as carrier gases. The substrates used in this experiment were double-polished α -Al₂O₃ (0001) wafers. The growth temperatures for the GaN buffer and single crystal epilayer were 550 °C and 1020 °C, respectively. During the MOCVD process, the flow rates of the TMG, DEZn, NH₃, H₂ and N₂ were 20 $\mu\text{mol min}^{-1}$, 3 $\mu\text{mol min}^{-1}$, 3.5 sl min^{-1} , 0.5 sl min^{-1} and 0.5 sl min^{-1} , respectively. The thicknesses of the GaN samples, measured by cross-section microscopy, were in the range of 2–3 microns.

The FTIR-GIRA measurements were carried out using a MAGNA-IR 750 spectrometer (Series II) with the grazing incidence angle fixed at 80°. The resolution was 4 cm^{-1} and the number of scans was 32. All spectra were measured at room temperature and expressed as absorbance vs. wavenumber.

The radioactive element ⁶⁰Co was used as a source of gamma rays with a photon energy of 1.25 MeV. The GaN films were irradiated in air at room temperature with a dosage of 0.60 MGy. Before irradiation, the electron Hall mobility and electron concentration of the GaN samples were 60–80 $\text{cm}^2 \text{Vs}^{-1}$ and $5\text{--}7 \times 10^{17} \text{ cm}^{-3}$, respectively. They changed little in the irradiation process.

3. Results and discussion

In figure 1, curves (a) and (b) show the FTIR-GIRA spectra for a Zn-doped GaN film before and after the gamma-ray irradiation, respectively, in the wavenumber range from 3500 to 2500 cm^{-1} . Before irradiation, three weak peaks at 2850, 2925 and 2960 cm^{-1} in spectrum (a) can be observed. Yi *et al* [6] reported three absorption peaks at 2853, 2923 and 2956 cm^{-1} in Mg-doped GaN, which are identified as due to stretching of the LVMs of C–H in CH_{*n*} with *n* = 1, 2 and 3, respectively. The wavenumbers of the three peaks in spectrum (a) of figure 1 are very close to those reported by Yi *et al* [6], and hence can be assigned to the same origins.

After gamma-ray irradiation, an enhancement in intensity of the FTIR-GIRA spectrum and a series of new absorption features were observed, as shown in spectrum (b) of figure 1. Each peak of the C–H LVMs in the spectrum discussed above increased markedly in intensity with a little shift in wavenumber, e.g., after irradiation the 2925 and 2850 cm^{-1} peaks shifted to 2922 and 2846 cm^{-1} , respectively. Moreover, two stronger peaks at 2951 and 2961 cm^{-1} in spectrum (b) appeared instead of the weak peak at 2960 cm^{-1} in spectrum (a). Four new absorption peaks at 3440, 3355, 3174 and 3088 cm^{-1} in the wavenumber range of 3500–3000 cm^{-1} and three new absorption peaks at 2819, 2712 and 2610 cm^{-1} in the range of 2500–3000 cm^{-1} appeared clearly in spectrum (b) of figure 1.

In figure 2, curves (a) and (b) show the FTIR-GIRA spectra for the Zn-doped GaN film

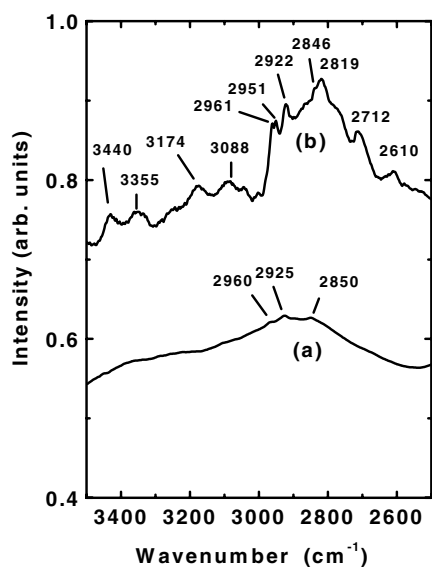


Figure 1. FTIR-GIRA spectra from a Zn-doped GaN film in the 3500 to 2500 cm^{-1} wave number range (a) before and (b) after gamma-ray irradiation.

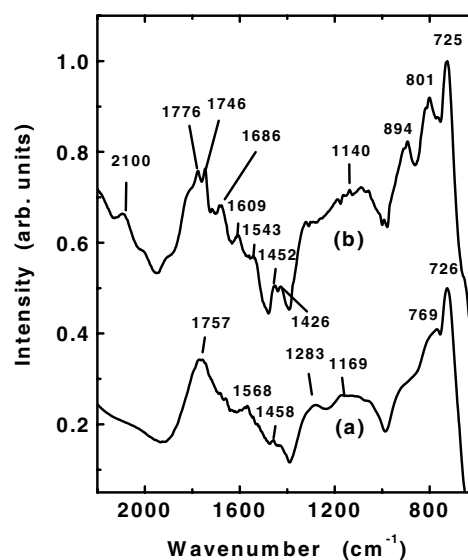


Figure 2. FTIR-GIRA spectra from a Zn-doped GaN film in the 2200 to 600 cm^{-1} wave number range (a) before and (b) after gamma-ray irradiation.

before and after the gamma-ray irradiation, respectively, in the range from 2200 to 600 cm^{-1} . As shown in spectrum (a) of figure 2, before irradiation, five features at 1757, 1568, 1458, 769 and 726 cm^{-1} and two broad bands around 1283 and 1169 cm^{-1} can be clearly observed. After irradiation, many more features with wave numbers at 2100, 1776, 1746, 1686, 1609, 1543, 1452, 1426, 1140, 894, 801 and 725 cm^{-1} appeared, as apparent in spectrum (b) of figure 2.

In Zn-doped GaN, some deep states were identified at 0.21 (E_{A1}), 0.34 (E_{A2}), 0.65 (E_{A3}), 1.02 (E_{A4}) and 1.42 (E_{A5}) eV above the top of the valence band (E_V) [13]. The three absorption regions of 2600–3000 cm^{-1} in figure 1, and of 1000–1400 and 1450–1900 cm^{-1} in figure 2, may be also related to the transitions $E_{A2}-E_V$, $E_{A2}-E_{A1}$, and $E_{A1}-E_V$, respectively. The distributions of the deep states could be affected by material defects and modified by gamma-ray irradiation, which may in turn result in some fine structures in the absorption regions.

Hydrogen as a carrier gas is always introduced in the GaN growth process. Most hydrogen atoms in the GaN films before gamma-ray irradiation are in either an IR inactive state or very weak IR activated state (such as in hydrogen molecules). In GaN films gamma-ray irradiation can generate atomic hydrogen as well as defects. The atomic hydrogen has a very high diffusion coefficient [14], so it can combine with impurities, defects including those induced in irradiation and unsaturated radicals, such as CH_n ($n = 1, 2$ and 3) and NH_n ($n = 1, 2$), to cause new H-related complexes. During the MOCVD process, carbon contamination is hardly avoidable due to the dissociation of TMG and DEZn that leads to the presence of the CH_n ($n = 1-3$) group; the incomplete decomposition of NH_3 may also produce NH_n ($n = 1, 2$) groups in GaN films.

The features with frequencies higher than 1500 cm^{-1} shown in figures 1 and 2 most probably originate from vibrational modes of complexes of H, which is the lightest element in the periodic table. Discussion and possible identification of some new features in both figures are given as follows:

(a) The 2819 cm^{-1} peak in spectrum (b) of figure 1: we note that the strong 2819 cm^{-1} peak

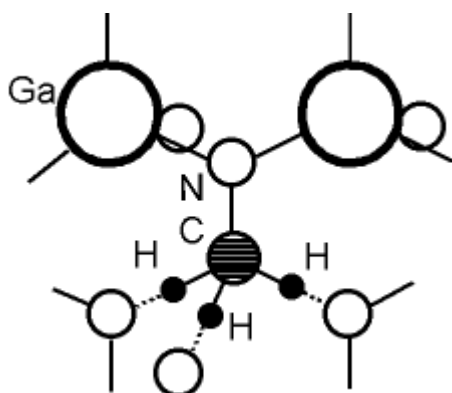


Figure 3. A possible configuration for the N-CH₃ complex in a GaN lattice.

is located in a wavenumber range of 2810–2820 cm⁻¹ of the C–H stretching vibration of an N–CH₃ radical [15]. Thus, the 2819 cm⁻¹ peak most probably originates from a C–H stretching LVM of an N–CH₃ radical in GaN, for which a possible configuration is proposed in figure 3. A C atom substitutes for a Ga atom in the GaN lattice and bonds to three H atoms and a neighbouring N atom, with each of the three hydrogen bonds formed with the H atom at the bond center site between the C atom and a neighbouring N atom.

- (b) The 3174, 3355 and 3440 cm⁻¹ peaks in spectrum (b) of figure 1: the peak with a frequency of 3174 cm⁻¹ observed in figure 1 is close to the previously reported stretching vibrational frequency of 3125 cm⁻¹ for the N–H in Mg-doped GaN. Hence, the 3174 cm⁻¹ mode may presumably correspond to the stretching vibration of N–H neighbours to Zn_{Ga} in GaN. On the other hand, the calculated stretching mode of N–H neighbours to Mg_{Ga} in GaN has been reported to be 3360 cm⁻¹ [16]. Thus, the observed 3355 cm⁻¹ peak in figure 1 can also be a candidate of the stretching mode of N–H neighbours to Zn_{Ga}. Recently, Van de Walle calculated the vibrational frequencies for a family of V_{Ga}H_n complexes [17]. The calculated H stretching modes are 3100 cm⁻¹ in V_{Ga}H and 3470 cm⁻¹ in V_{Ga}H₄ complexes. A larger number of hydrogen atoms in the V_{Ga}H_n complexes leads to shorter N–H bonds and higher vibrational frequencies. It seems reasonable to assign the observed 3440 cm⁻¹ peak in spectrum (b) of figure 1 to the H stretching mode in the V_{Ga}H₄ complex. Collectively, we ascribe the 3174, 3355 and 3440 cm⁻¹ peaks to be LVMs of N–H with different neighbours.
- (c) The 1426 and 894 cm⁻¹ peaks in spectrum (b) of figure 2 and the 3088 cm⁻¹ peak in spectrum (b) of figure 1: reference [15] reported the frequencies of in-plane deformation (scissoring) and out-of-plane wagging C–H vibrations in a vinyl group. The former is in the ranges of 1412–1420, 1397–1429 or at 1425 cm⁻¹, while the latter is in the range of 885–895 or at 890 cm⁻¹. The 1426 and 894 cm⁻¹ peaks in spectrum (b) of figure 2 just have frequencies located, respectively, in the ranges of 1397–1429 cm⁻¹ and 885–895 cm⁻¹ and hence are considered to originate, respectively, from in-plane scissoring and out-of-plane wagging vibration modes of C–H in a vinyl group in GaN, as shown in figure 4 where R is either an N or a Ga atom in a GaN lattice. Reference [15] also reported the frequency of a C–H stretching vibration mode of a vinyl group to be 3080 cm⁻¹, to which the frequency of the 3088 cm⁻¹ peak in spectrum (b) of figure 1 is very close. Hence, we believe the LVM at 3088 cm⁻¹ most probably comes from a C–H stretching vibration of a vinyl group in GaN.

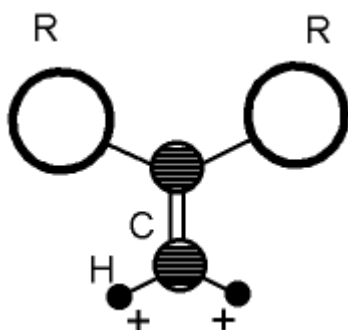


Figure 4. A possible configuration for a vinyl group in GaN, where R is either an N or a Ga atom in a GaN lattice.

- (d) The 2100 cm^{-1} peak in spectrum (b) of figure 2: besides carbon and hydrogen, Si is another widely studied common impurity in GaN [2, 14] arising most probably from the quartz reactor in a MOCVD system [2, 18]. A 2090 cm^{-1} LVM in hydrogenated amorphous Si was ascribed to SiH_2 [19] and a 2100 cm^{-1} LVM in porous Si to Si–H in SiH_n complexes [20]. We tentatively assert that the 2100 cm^{-1} peak reported here could arise from Si–H or SiH_2 in the GaN.
- (e) The 1776 , 1757 and 1746 cm^{-1} peaks in figure 2: Duan *et al* reported an absorption band around 1730 cm^{-1} and ascribed it to the Ga–H (beside an N vacancy) LVM in GaN [21]. The 1757 cm^{-1} peak in spectrum (a) and the 1746 and 1776 cm^{-1} peaks in spectrum (b) of figure 2 have frequencies close to 1730 cm^{-1} , and hence may have the same origin. The small differences in vibration frequency among these LVMs may be attributed to differences in the microenvironment of the Ga–H, such as the defects nearby.
- (f) The 2712 cm^{-1} peak in spectrum (b) of figure 1: in the FTIR-GIRA spectrum of a C-implanted GaN sample [22], both the 2712 and 2819 cm^{-1} peaks (the latter has been discussed in (1)) appeared simultaneously. However, for a GaN control sample without C implantation neither peak was observed. This result indicates that the 2712 cm^{-1} peak is probably C-related.

It should be noted that the absorptions of LVMs are relatively narrow with $10\text{--}20\text{ cm}^{-1}$ full width at half maximum in the general case. The broadening of some assigned LVMs peaks in this paper may presumably be due to gamma-ray irradiation, FTIR-GIRA measurement and other reasons.

From the discussions we can see that gamma-ray irradiation combined with FTIR-GIRA is an effective method for studying the LVMs, especially those related to H, in GaN films.

4. Conclusion

We report that gamma-ray irradiation can introduce new features with wavenumbers such as 3440 , 3355 , 3174 , 3088 , 2819 , 2712 , 2100 , 1426 and 894 cm^{-1} in the FTIR-GIRA spectra of GaN. The 3174 , 3355 and 3440 cm^{-1} peaks are ascribed to be the LVMs of N–H with different neighbours. The 2819 cm^{-1} LVM can be assigned to a C–H stretching vibration in an N– CH_3 complex, and the 894 , 1426 and 3088 cm^{-1} LVMs to, respectively, out-of-plane wagging, in-plane scissoring and stretching C–H vibrations in a vinyl group in GaN. It is demonstrated that gamma-ray irradiation combined with FTIR-GIRA is an effective method for studying the LVMs, especially those related to H, in GaN films.

Acknowledgments

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