Defect-induced Raman scattering in resonance with yellow luminescence transitions in hexagonal GaN on a sapphire substrate

De-Sheng Jiang,[a] M. Ramsteiner,[b] and K. H. Ploog
Paul Drude Institute for Solid State Electronics, Hausvogteiplatz 5-7, D-10117 Berlin, Germany

H. Tews, A. Graber, R. Averbeck, and H. Riechert
Siemens Corporate Research and Development, D-81730 Munich, Germany

Strong defect-specific low-frequency peaks are detected in low-temperature Raman spectra of hexagonal GaN grown by molecular beam epitaxy on sapphire substrate. The intensity of these peaks is found to be enhanced by excitation in resonance with yellow luminescence transitions. The validity of the assignment to electronic Raman scattering (ERS), as proposed before for their counterparts in cubic GaN on GaAs [M. Ramsteiner, J. Menniger, O. Brandt, H. Yang, and K. H. Ploog, Appl. Phys. Lett. **69**, 1276 (1996)], is confirmed. Our results imply that the observed ERS peaks are related to shallow donors which are not necessarily hydrogenic. One Raman peak at very low frequency (11.7 meV) is alternatively explained by a pseudo-localized vibrational mode. © *1998 American Institute of Physics.* [S0003-6951(98)03903-5]

The search for the origin of the n-type conductivity in nominally undoped GaN is an important issue for research.[1] Therefore, any spectroscopic assignment of donors in GaN is highly desirable. Electronic donor transition induced Raman excitations in molecular beam epitaxy (MBE) grown GaN on GaAs was first reported by Ramsteiner *et al.*[2] The corresponding Raman peaks are located in the energy range between 18.5 and 30 meV. They are observed for excitation in resonance with yellow luminescence transitions, i.e., far below the fundamental band gap. Peaks at 23.4 and 29.4 meV have been attributed to electronic Raman scattering (ERS) caused by internal shallow donor transitions.[2,3] Siegle *et al.*[4] reported ERS Raman peaks in the same energy region and claimed, however, that these peaks are only observable for GaN on GaAs but not for hexagonal GaN on sapphire. We have comprehensively investigated low-temperature Raman spectra of gas-source MBE GaN layers grown on both sapphire and GaAs substrates. A whole set of the investigated GaN-on-sapphire samples indeed shows strong and sharp Raman peaks in the low-energy region which can be attributed to electronic excitations of donors which are involved in yellow luminescence transitions. The obtained results, however, imply that the donors involved are not necessarily hydrogenic. We show that two peaks have their counterparts in Raman spectra of cubic GaN.[2]

The investigated hexagonal GaN samples were grown on (0001)-oriented sapphire substrates using MBE with a rf plasma assisted nitrogen gas source. The typical growth conditions have been successfully employed for preparing high quality starting GaN layers in entirely MBE grown quantum well blue and green light-emitting diode (LED) structures.[5] The 1-μm-thick GaN samples were grown on GaN buffer layers under slightly Ga-rich conditions. The carrier concentration in the nominally undoped samples is of the order of 10^{17} cm^{-3} and the mobility a value of 300 cm^2 V/s. Photoluminescence measurements show strong excitonic peaks in the near band edge region. In addition, a series of samples was investigated for which the MBE growth parameters of the GaN sample or the buffer layer have been intentionally varied. The Raman spectra were measured with a Dilor triple monochromator Raman system in a backscattering configuration by using different polarization geometries.[2] The measurements were performed by using confocal micro-Raman equipment in which the light spot is focused by a microscope to a diameter of 2 μm.

Figure 1 depicts polarized low-temperature Raman spectra of a GaN-on-sapphire sample and of a GaN-on-GaAs sample[2] for an incident photon energy of 2.41 eV. The lattice phonon lines in the spectra reflect the dominant crystal phases of the samples. The strong E_2 phonon line in the GaN-on-sapphire sample is characteristic of hexagonal GaN, while the relatively strong TO phonon line indicates that the GaN layer on GaAs is predominantly cubic.[6] The crucial point is the observation of additional peaks in the low-energy range between 10 and 30 meV of both spectra. Actually, a whole series of the investigated GaN-on-sapphire samples shows five strong Raman peaks located at 11.7, 18.3, 23.4, 27.1, and 30.7 meV marked by γ, $A*$, α, $B*$, and β, respec-
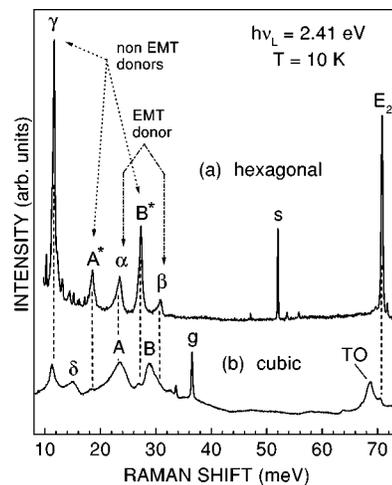

FIG. 1. Low-temperature Raman spectra of a hexagonal GaN-on-sapphire sample (a) and a predominantly cubic GaN-on-GaAs sample (b) (Ref. 3). The optical phonon lines of the sapphire (s) and GaAs (g) substrates are indicated. Excitation was at 2.41 eV.

[a] On leave from Institute of Semiconductors, CAS, Beijing 100083, People's Republic of China.
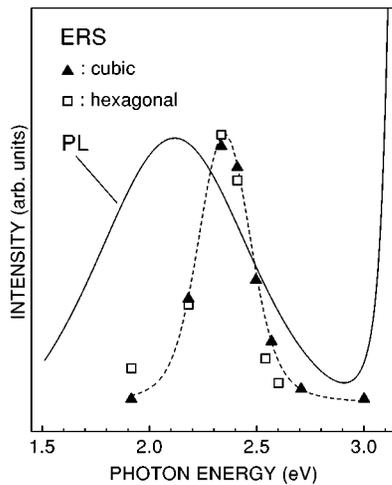[b] Electronic mail: mer@pdi.wias-berlin.de

FIG. 2. Intensity of electronic Raman scattering (ERS) as a function of the incident photon energy for cubic (integrated intensity of peaks A and B) (Ref. 2) and hexagonal GaN samples (integrated intensity of peaks α, $A*$, and $B*$) as well as a spectrum of the yellow luminescence (PL) taken at 10 K.

tively (see Fig. 1). There peak β is split in some samples. All peaks are resonantly enhanced for excitation with green light and decreased in intensity for increasing temperature. The notation of peaks $A*$ and $B*$ follows Ref. 2 where these peaks, observed in Raman spectra of GaN on GaAs, were attributed to the contribution of hexagonal GaN crystallites. The detection of strong $A*$ and $B*$ peaks in the GaN layers grown on sapphire justifies the previous assignment to the hexagonal phase.[2] It is noticeable that for the GaN-on-sapphire system the contamination with As can be neglected. Therefore, we exclude any connection of the low-energy peaks with GaAs as concluded in Ref. 4 where either N impurities in GaAs or As defects in GaN have been proposed as the origin of these peaks.

One striking feature of the low-energy Raman peaks is that their intensities are strongly dependent on the incident photon energy. Figure 2 shows the spectral dependence of their integrated intensity normalized to the E_2 phonon line intensity for a GaN-on-sapphire sample. For comparison a typical yellow luminescence band is also displayed in Fig. 2. It is found that the maximum Raman scattering efficiency occurs at a photon energy of approximately 2.35 eV, i.e., far below the band gap of GaN but quite close to the peak energy of the yellow luminescence in GaN at nearly 2.1 eV. The observed resonance effect is similar to that observed in GaN-on-GaAs samples[2] and is attributed to yellow luminescence transitions between shallow donors and deep acceptors. It is important to note that such a resonance profile measurement is a sensitive way to get information about absorption transitions inside the band gap. In contrast, low-temperature photoconductivity measurements of GaN layers often reveal only a changing slope of the spectral response in the energy range below the band edge of GaN, but no absorption peak.[7]

A careful inspection of Fig. 1 reveals that the frequencies of peaks α and β are very close to those of peaks A and B in cubic GaN, which have been assigned to shallow donor electronic transitions in cubic GaN.[2] Peak α almost coincides

with peak A while the frequency of peak β is very close to but slightly higher than that of peak B. Their line shapes are asymmetric like those of peaks A and B. Theoretical calculations predict that between cubic and hexagonal GaN there is only a minor difference in the electronic structure and defect formation energies.[8] Therefore, it is reasonable to assume that peaks α and β are the hexagonal counterparts of peaks A and B with the small differences in the peak positions caused by the different energy band parameters of the two GaN phases. Consequently, peaks α and β can be attributed to $1s-2s$ and $1s-3s$ transitions of hydrogenic shallow donors with an ionization energy of 33 meV. This value agrees well with experimental values and with the estimate from the effective mass theory (EMT) for hexagonal GaN.[9]

The low-energy Raman peaks γ, α, β, $A*$, and $B*$ observed in the GaN-on-sapphire system are most probably related to impurities since they are not observed in all samples of comparable quality. Strong low-energy Raman peaks have been observed only in the part of the investigated MBE grown GaN sample series having carrier concentrations in the order of 10^{17} cm^{-3}, which implies that the position of the Fermi level and hence the charge state of shallow donors is important for observing these peaks. A preliminary secondary ion mass spectroscopy (SIMS) analysis was performed for the GaN layers on sapphire. Comparing samples which show weak and strong low-energy Raman peaks, respectively, a higher content of residual Si is found for the latter. This result suggests that Si might be responsible for at least part of the observed Raman processes. Actually, different binding energies between 12 and 35 meV, obtained from Hall effect measurements, have been related to Si donors in hexagonal GaN.[10,11] However, a coincidental high O content in the samples with large Si concentrations cannot be excluded from our SIMS measurements. Furthermore, the concentration of the deep acceptors involved in the resonance scattering process[2] might be important for the observability of the low-energy Raman peaks. Therefore, further work is necessary to identify the chemical nature of the residual impurities.

The dependence of the Raman intensity of peaks γ, $A*$, and $B*$ on the incident photon energy is similar to that of peaks α and β (see Fig. 2). As can be clearly seen in Fig. 3, the temperature dependence of the intensities of peaks γ, $A*$, and $B*$ is also similar to that of peaks α and β. They decrease with increasing temperature and almost completely disappear close to room temperature. The relatively sharp peaks γ, $A*$, and $B*$ apparently have no counterpart in cubic GaN and are therefore specific for the hexagonal phase.[2] An interesting fact is that the intensity ratio between peak $A*$ and peak $B*$ is found to be nearly constant in all samples (close to 1:2), although in general the relative intensities of the different peaks vary somewhat from sample to sample. A careful examination of peaks $A*$ and $B*$ observed in different GaN-on-GaAs samples[2,4] also reveals nearly the same intensity ratio. These two peaks were tentatively assigned to EMT type donor transitions in hexagonal GaN assuming a binding energy of approximately 27 meV.[2] However, the consistency of the observed peak energies with those predicted by EMT is not as good as in the case of peaks α and β, making it more likely that peaks $A*$ and $B*$ are due to
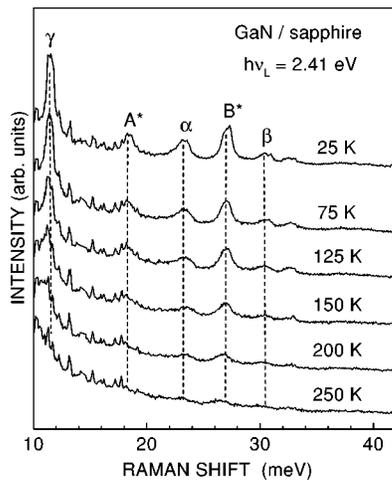
FIG. 3. Raman spectra of a hexagonal GaN-on-sapphire sample for different sample temperatures indicated in the figure. Excitation was at 2.41 eV.

electronic excitations of different donor species. Consequently, assuming peaks γ, A^*, and B^* to be caused by lowest-energy electronic transitions of different donors, the corresponding binding energies—given by EMT values and a shift due to central cell correction—are 20, 26.5, and 35.5 meV. In fact, three such binding energies, derived from electrical and optical measurements, have already been reported for different donors in GaN.[9–12] Actually, these donors do not necessarily have to be hydrogenic.

An alternative explanation of peaks γ, A^*, and B^* is to correlate them with defect-induced pseudo-local vibrational modes. Such an assignment is regarded in particular for peak γ since its peak energy is much lower than expected from EMT for lowest-energy electronic transitions. For vibrational modes, the decrease in peak intensity at higher temperatures might be explained by the enhanced damping of vibrations via their coupling to lattice phonon modes, which also causes the broadening of the Raman peak with increasing temperature (see Fig. 3). Resonant Raman scattering of defect vibrational modes with frequencies in the vicinity of the acoustic phonon branches has already been reported by Berg et al.[13] In fact, some spectral features of peaks γ, A^*, and B^* are different from those of α and β. For example, the temperature-induced energy shift $\Delta\omega$ of the peak positions between 15 K and room temperature is 0.75 meV instead of 0.2 meV. This frequency shift is comparatively large, but is not in conflict with the possible assignment to pseudo-local vibrational modes. The frequency of local vibrational modes could have a remarkable temperature-induced change depending on the anharmonic terms.

However, we suppose that peaks γ, A^*, and B^* are induced by electronic transitions instead of vibrational modes since the temperature dependence of their peak intensities is difficult to explain for pseudo-local vibrational modes, but can be well understood for electronic Raman excitations which are dependent on the thermal ionization of donors. Moreover, these peaks fall in the frequency region of the acoustic phonon branches in GaN close to the maximum of the phonon density of states (DOS).[14] This overlap of the vibration frequencies would cause a rapid decay of the defect vibrational modes resulting in a severe broadening of the

Raman peaks and a decrease in peak intensity. Such a strong broadening was not observed in our experiments, as shown in Fig. 3. In contrast to the case of vibrations, the resonant coupling between electronic excitations and acoustic phonons should be much weaker because the elastic vibrational modes will not induce a large electron–phonon interaction. The above arguments support our assignment to electronic excitations for peaks γ, A^*, and B^*. Their spectral features imply that they are caused by electronic transitions between the energy levels of donor species which are not necessarily hydrogenic centers. For example, these donors may be induced by strongly localized deep centerlike defects in GaN. Their electronic levels deviate from the usual EMT ones as predicted by calculations.[8] A possible candidate could be the O donor, for which DX-type behavior associated with a strongly localized state has been found in hexagonal but not in cubic GaN.[15,16]

In conclusion, Raman scattering measurements on MBE grown GaN-on-sapphire samples revealed low-energy peaks which are enhanced for excitation in resonance with yellow luminescence transitions. These peaks are found to be specific for the hexagonal phase and—in analogy to earlier work on cubic GaN (Ref. 2)—we attribute them to electronic excitations of donors. In addition, an alternative explanation as a quasi-local vibrational mode is given for the Raman peak lowest in energy (11.7 meV). After further work on the chemical origin of the different Raman peaks they could be used as spectroscopic fingerprints for different donor species in GaN.

[1] See, e.g., S. Strite and H. Morkoc, J. Vac. Sci. Technol. B **10**, 1237 (1992), and references therein.

[2] M. Ramsteiner, J. Menniger, O. Brandt, H. Yang, and K. H. Ploog, Appl. Phys. Lett. **69**, 1276 (1996).

[3] M. Ramsteiner, J. Menniger, O. Brandt, H. Yang, and K. H. Ploog, Appl. Phys. Lett. **70**, 910 (1997).

[4] H. Siegle, I. Loa, P. Thurian, L. Eckey, A. Hoffmann, I. Broser, and C. Thomsen, Appl. Phys. Lett. **70**, 909 (1997).

[5] H. Tews, R. Averbeck, A. Graber, and H. Riechert, Electron Lett. **32**, 2004 (1996).

[6] M. Giehler, M. Ramsteiner, O. Brandt, H. Yang, and K. Ploog, Appl. Phys. Lett. **67**, 733 (1995).

[7] C. H. Qiu, C. Hoggatt, W. Melton, M. W. Leksono, and J. I. Pankove, Appl. Phys. Lett. **66**, 2712 (1996).

[8] J. Neugebauer and C. G. Van de Walle, Phys. Rev. **50**, 8067 (1994).

[9] B. K. Meyer, D. Volm, A. Graber, H. C. Alt, T. Detchprohm, A. Amano, and I. Akasaki, Solid State Commun. **95**, 597 (1995).

[10] W. Götz, M. Johnson, C. Chen, H. Liu, C. Kuo, and W. Imler, Appl. Phys. Lett. **68**, 3144 (1996).

[11] P. Hacke, A. Maekawa, N. Koide, K. Hiramatzu, and N. Sawaki, Jpn. J. Appl. Phys., Part 1 **33**, 6443 (1994).

[12] S. Fischer, D. Volm, D. Kovalev, B. Averboukh, A. Graber, H. C. Alt, and B. K. Meyer, Mater. Sci. Eng. B **43**, 192 (1997).

[13] R. S. Berg, P. Y. Yu, and E. R. Weber, Appl. Phys. Lett. **47**, 515 (1985); R. S. Berg and P. Y. Yu, Phys. Rev. **33**, 7349 (1986).

[14] H. Siegle, L. Filippidis, G. Kaczmarczuk, A. P. Litvincuk, A. Hoffmann, and C. Thomson, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors,* edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), p. 537.

[15] C. Wetzel, T. Suski, J. W. Ager III, E. R. Weber, E. E. Haller, S. Fischer, B. K. Meyer, R. J. Molnar, and P. Perlin, Phys. Rev. Lett. **78**, 3923 (1997).

[16] C. G. Van de Walle and J. Neugebauer (unpublished).