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Exciton Spectra of Cubic and Hexagonal GaN Epitaxial Films

Shigefusa CHICHIBU[1,2], Hajime OKUMURA[2], Guy FEUILLET[2], Shuji NAKAMURA[3], and Sadafumi YOSHIDA[2]

[1]*Faculty of Science and Technology, Science University of Tokyo, 2641 Yamazaki, Noda, Chiba 278, Japan*

[2]*Materials Science Division, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan*

[3]*Nichia Chemical Industries Ltd., 491 Oka, Kaminaka, Anan, Tokushima 774, Japan*

Exciton resonance energies of cubic (c-) and hexagonal (h-) GaN epitaxial films were determined by means of the modulated-photoreflectance (PR) measurements. The fundamental exciton resonance energy of c-GaN, namely 3.257 eV at 10 K under the tensile biaxial strain, was confirmed to be smaller by about 0.2 eV than that of h-GaN. The temperature coefficient of the exciton energy in both polytypes was almost the same. Photoluminescence (PL) peaks due to recombination of excitons were found in both films. The E_2 phonon replicas of bound and free excitons were found in the low-temperature PL spectra of h-GaN. The increase of the linewidth of the excitonic PL peak caused by the increase of temperature was explained to be due to exciton-phonon coupling. The phonon predominantly acting on this behavior was considered as the lower-frequency blanch of E_2 and the longitudinal-optical E_1 modes for low and high temperature regime, respctively.

1. Introduction

Recent rapid progress in researches on optoelectronic applications of GaN and related nitrides[1)] has realized the superbright green- and blue-color InGaN single-quantum-well light emitting diodes (SQW-LED),[2)] current-injection stimulated emission from AlGaN/GaN double-heterostructure (DH),[3)] and room-temperature pulse oscillation of InGaN-based multi-quantum-well laser diodes (MQW-LD).[4)] Therefore the group-III nitrides have attracted intensive attention as suitable materials for short-wavelength light emitters. They are also hopeful to realize ultraviolet detectors and cold cathodes as much as high-temperature and/or high-power transistors due to thier higher stability.[1)]

Though much interest has been concentrated on the hexagonal (h-) polytype of GaN having the wurtzite structure, cubic (c-) potytype of GaN having the zincblende structure has also been grown by metalorganic vapor phase epitaxy (MOVPE)[5,6)] and gas-source molecular beam epitaxy (GSMBE).[7,8)] Physical and electronic properties of c-GaN have been investigated by several authors,[5-12)] because the cubic polytype may have superior electronic properties resulting from reduced phonon scattering in the higher symmetry crystal[13)] and it may have smaller effective masses than the hexagonal one. In addition, it can be cleaved along with the substrate facet, which enables us to prepare mirrors for the LD cavity easily.

Recently, exciton resonance energies in high-quality h-GaN films have been measured as a function of biaxial strain[14)] by means of modulated-photoreflectance (PR)[15)] measurements. A certain contribution of excitons has been found in PR and photoluminescence (PL) spectra of h-GaN even at room temperature (RT).[16)] However, there still remain unclear characteristics of excitons in c- and h-GaN heteroepitaxial layers. For example, the reported values for the energy gap of c-GaN[7-12)] scatter from 3.2 eV[9)] to 3.52 eV.[8)] Recently, Ramirez-Flores *et al.*[17)] have measured the PR spectra of c-GaN as a function of temperature, and have determined the band gap energy as 3.302 eV at 10 K. Okumura and Yoshida[18)] have also confirmed the exciton-gap eneregy of c-GaN as 3.26 ± 0.01 eV[7)] by means of the magnetic circular dichroism measurements. Menniger *et al.*[19)] have reported emissions due to free and bound exciton recombinations at 3.272 and 3.263 eV, respectively, in quasi-unstrained c-GaN films at 5 K. Therefore it is important to verify the exciton energy of c-GaN. We also would better to examine the effects of strain on excitons and the interaction of excitons with phonons.

In this work, exciton resonance energies of cubic (c-) and hexagonal (h-) GaN heteroepitaxial layers were determined as a function of temperature by means of PR measurements. PL spectra of both polytypes were measured, and the origin of the PL peak was discussed.

2. Experiments

The measured samples were 2-4 μ m-thick h-GaN(0001) epilayers, which were grown on sapphire substrates by MOVPE,[2,4)] and 0.12-0.2 μ m-thick c-GaN(001) epilayers, which were grown on 20 μ m-thick 3C-SiC/Si(001) by GSMBE using the electron-cyclotron resonance nitrogen plasma. The 3C-SiC substrates were grown by chemical vapor deposition using silane-propane-hydrogen reaction gas system at 1350℃.

In measuring PL spectra, the 325 nm line of a cw He-Cd laser was used as an excitation source. The PL signal was dispersed by a 67-cm focal length grating monochromator and was detected by the photomultiplier. The accuracy and resolution of the system was 0.5 and 2 meV, respectively, at a wavelength of 350 nm. The He-Cd laser was also used as a pump light for PR measurements. PR spectra were taken in near-normal reflection angle. To analyze the PR spectra simply,[20] the measurements were performed in the low-field regime. All measurements were carried out from 10 K to RT.

3. Results and Discussion

Three separate A, B, and C exciton resonance energies of the 4 μ m-thick h-GaN, which suffers compressive biaxial strain, are determined as 3.488, 3.496, and 3.531 eV

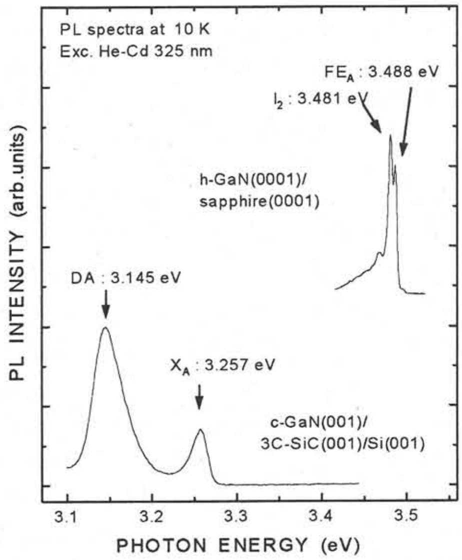

Fig.1 PL spectra at 10 K of c-GaN/3C-SiC and h-GaN/sapphire

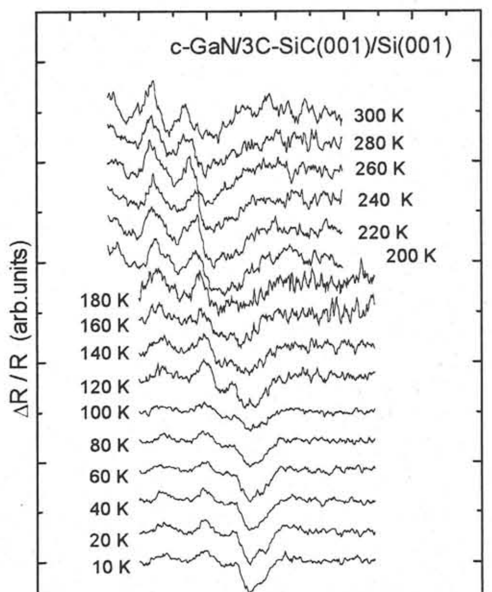

Fig.2 PR spectra of c-GaN/3C-SiC vs. temperature

at 10 K.[14] The PL peak energies of A and B free exciton emissions agree with the exciton resonance energies obtained from the PR spectra up to RT.[16] The value of the spin-orbit splitting of h-GaN is estimated to be about 16meV,[14] which is comparable to the value of c-GaN (17 meV),[17] and the results may reflect the N2p nature of the valence bands. The A exciton energy in unstrained h-GaN is deduced to be 3.471 eV at 10 K.[14]

The typical representatives of the PL spectra of c- and h-GaN at 10 K are shown in Fig.1. In contrast to the sharp PL lines from h-GaN, PL spectrum of c-GaN exhibits broader PL peaks at 3.257 and 3.145 eV. From the analysis of the PR spectra[14,16,20] shown in Fig.2, the exciton energy of c-GaN is estimated to be about 3.26 eV at 10 K, and the value agrees with the PL peak energy of X_A in Fig.1. Therefore X_A is assigned as an exciton-related emission from c-GaN. The obtained exciton resonance energy of c-GaN (3.26 eV at 10 K) is consistent with the exciton[7,18,19] and band gap[17] energies reported previously. The dwonshift of the exciton resonance energy (by 12 meV) in our thin c-GaN layer compared with the unstrained c-GaN (3.272 eV)[19] may be originated from the residual tensile biaxial strain caused by the difference of the thermal expansion coefficients between c-GaN and 3C-SiC/Si structure. It is noted from Fig.1 that the PL spectrum of our c-GaN epilayer does not exhibit the emission signals from h-GaN domains, which are frequently formed in c-GaN epilayers.

Because of the relatively large broadening of the exciton structure in the PR spectra, spin-orbit splitting of c-GaN cannot be determined in our experiment. However, it is confirmed that the exciton energy of c-GaN is about 0.2 eV smaller than that of h-GaN. Some extra structure in the

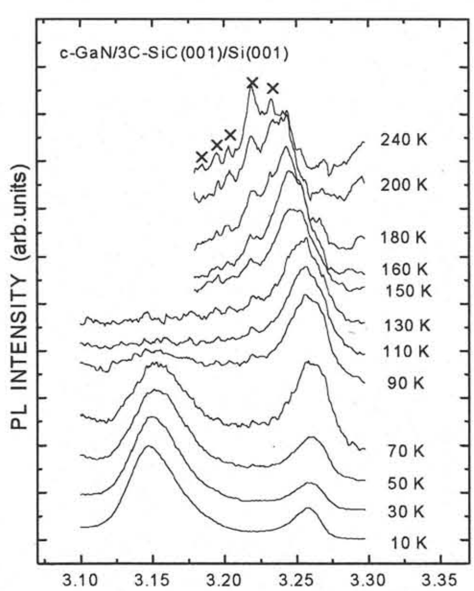

Fig.3 PL sepctra of c-GaN vs. temperature

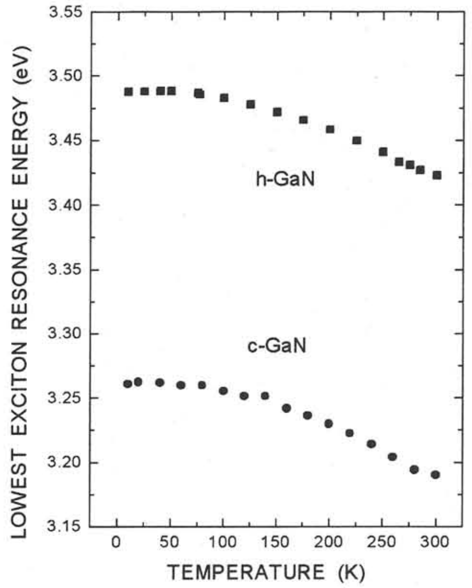

Fig.4 Lowest exciton resonance energy of c- and h-GaN vs. temperature

lower energy side is recognized in the PR spectra above 200 K, as shown in Fig.2, which might attributable to the strain or other effects.

The excitonic emission at 3.257 eV in c-GaN is observed up to 200 K, as shown in Fig.3. This result implies that exciton transition is dominant in c-GaN. Conversely the donor-acceptor pair recombination (3.145 eV)[19] vanishes at around 110 K. Further improvement of the film quality may enable us to observe excitonic emissions up to RT, as is the case with h-GaN.[16]

The lowest exciton energy of c- and h-GaN is plotted in Fig.4 as a function of temperature. The estimated temperature coefficients of exciton energies between 180 K and 300K for both polytypes are close to each other. The value is about $3.6\text{-}3.7\times10^{-4}$ eV/K.[16]

Though the data are not shown, the lower-frequency blanch of the E_2 phonon replicas of bound and free excitons (indicated in Fig.1by I_2 and FE_A,respectively) were found in the low-temperature PL spectra of h-GaN.[16] Increase of the full width at half maximum of the excitonic PL peak with increasing the temperature can reasonably explained to be due to exciton-phonon coupling. The phonon predominantly acting on this behavior is considered as the lower-frequency blanch of E_2 mode and the longitudinal-optical E_1 mode for low and high temperature regime, respctively. Therefore the strain in the epilayer is considered to affect not only the exciton resonance energy[14] but also the exciton-phonon coupling.

4. Conclusion

In summary, exciton resonance energies of h- and c-GaN heteroepitaxial films were compared. A remarkable difference of their exciton energy was confirmed from PR and PL measurements. Effects of strain on the exciton-related properies were briefly discussed.

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