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Raman Scattering Characterization of Annealed GaN_xAs_{1-x} Layers

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Raman scattering from the GaN_xAs_{1-x} layers grown on the (001) GaAs substrates has been investigated to characterize the locally ordered structures in the grown layers. New optical phonon modes from the confined GaAs and GaN structures and the disorder activated modes were observed. These new modes strongly suggest the presence of the trigonal $\{111\}$-$(GaN)_1(GaAs)_1$ natural superlattice cluster in the GaN_xAs_{1-x} layers. A thermal annealing effect has been also investigated through the variation of the confined GaAs- and the GaN-like modes and we have confirmed that the hydrogen (H) atoms included in the as-grown GaN_xAs_{1-x} layers desorb from the layers by the annealing. The results strongly indicate that the H-induced degradation in the natural superlattice cluster are recovered through breaking of the N-H bonds by the annealing.

KEYWORD: GaN_xAs_{1-x}, Raman scattering, natural superlattice cluster, thermal annealing, N-H bond

1. Introduction

GaN_xAs_{1-x} alloys have been intensively investigated to fabricate the III-V light-emitting devices for optical communication. They have peculiar properties compared with the conventional III-V alloys, such as a large red shift of bandgap energies. However, the crystal quality of reported GaN_xAs_{1-x} layers grown by MOMBE or MOVPE techniques rapidly degrade as increasing of the nitrogen (N) molar fractions. In the case of MOVPE growth, the PL intensity from the GaN_xAs_{1-x} layers dramatically increases by a thermal annealing after the growth. Recently, Tanaka et al. have reported that the hydrogen (H) atoms existed as the N-H bonds in the as-grown GaN_xAs_{1-x} layers are the origin of the PL intensity suppression[1)]. On the other hand, Mintairov et al. have reported that the formation of the trigonal $\{111\}$-$(GaN)_1(GaAs)_1$ naural superlattice (SL) cluster would be expected in the GaN_xAs_{1-x} systems from the results of Raman scattering observations[2)]. The Raman scattering spectroscopy is a sensitive technique to study the local structures of the impurity incorporations and the deviations from a long range order induced by the incorporation of the guest atoms. Therefore, the Raman scattering from the annealed GaN_xAs_{1-x} samples is very interesting. In this paper, we have reported the Raman scattering characterization for the as-grown and the annealed GaN_xAs_{1-x} layers to investigate the local structures such as the natural SL clusters in the annealed GaN_xAs_{1-x} layers.

2. Experimental

GaN_xAs_{1-x} samples were grown on the (001) GaAs substrates with 0.5μm (N:0.79%) and 1.9μm (N:1.2%) thickness by the low-pressure MOVPE with a horizontal reactor. The carrier gas was palladium-purified H_2 and triethylgallium (TEG), tertiarybutylarsine (TBAs) and dimethylhydrazine (DMHy) were used as reactants. Growth temperature was 500 °C (N:0.79%) and 480 °C (N:1.2%). The N molar fractions were estimated by X-ray diffraction (XRD) and secondary ion mass spectroscopy (SIMS)[3)]. The thermal annealing was performed for 10min in a flowing TBAs and H_2 ambient at 500 °C.

The microscopic Raman scattering measurements were carried out in the back scattering configuration at room temperature using the 632.8nm He-Ne laser. The power of incident laser beam on the sample was about 3mW. The Raman measurements were performed in the

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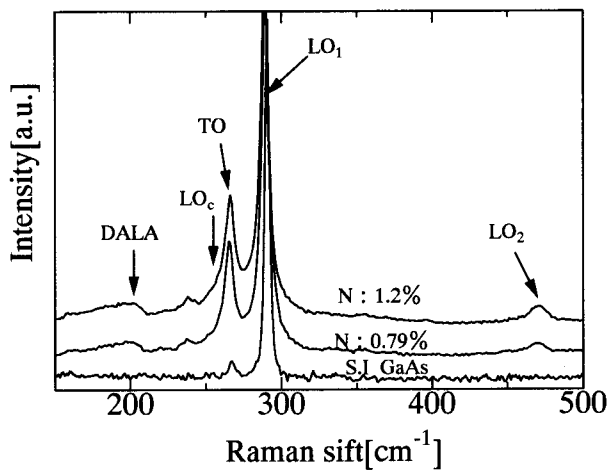

Fig. 1. Typical Raman spectra for a S.I.GaAs and the as-grown GaN_xAs_{1-x} layers (x=0.0079,0.012).

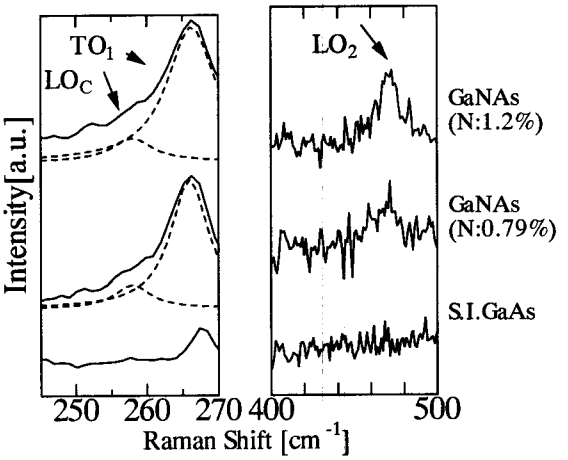

Fig. 2. Typical LOc, TO_1 and LO_2 Raman modes from a S.I.GaAs and the as-grown GaN_xAs_{1-x} layers (x=0.0079,0.012).

range from 100 to 700 cm^{-1} and the resolution was 1 cm^{-1}. A polarization rotator were used to measure the allowed $z(x,y)\bar{z}$ and the forbidden $z(x,x)\bar{z}$ modes (where the x // [100], y // [010] and z // [001]) in the backscattering configuration for the longitudinal-optical (LO) modes of the zincblende structure.

3. Results and discussions

Typical Raman spectra from a semi-insulator (S.I) GaAs substrate and the GaN_xAs_{1-x} as-grown layers are shown in Fig. 1. Longitudinal-optical (LO_1) and transverse-optical (TO_1) modes of the GaAs components were observed at 291cm^{-1} and 268cm^{-1}, respectively. A disorder activated longitudinal acoustic (DALA) mode that was induced by the disorder due to the N incorporations was also observed near 200cm^{-1} as shown in Fig. 1. Additionally, as shown in Fig. 2, a weak shoulder near 257cm^{-1} denoted by LOc on the low-wave-number side of TO_1 appeared only in the GaN_xAs_{1-x} samples and a newly clear phonon mode denoted by LO_2 was also observed near 470 cm^{-1}. The frequency of the observed LO_2 phonon mode which is very different from that of the bulk GaN (730cm^{-1}) corresponds with the reported GaN-like phonon mode in the GaN_xAs_{1-x} system by Mintairov et al.[2)]

Raman spectra of the LO_2 mode for the $GaN_{0.012}As_{0.988}$ samples measured in the $z(x,y)\bar{z}$ and the $z(x,x)\bar{z}$ configurations are shown in Fig. 3. Although the (x,x) LO component is forbidden in the zincblende structure with the T_d symmetry, the LO_2 mode is clearly observed even in the forbidden configurations, as shown in Fig. 3. According to Mintairov et al., the (x,x) component of the LO_2 mode indicates that the strong deviation from the

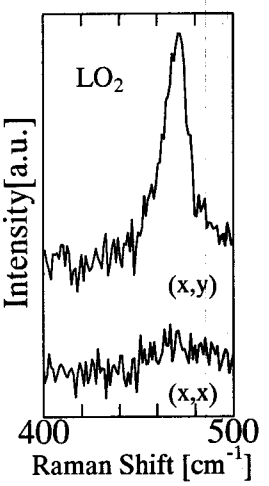

Fig. 3. Typical polarized Raman modes from the as-grown $GaN_{0.012}As_{0.988}$ layer.

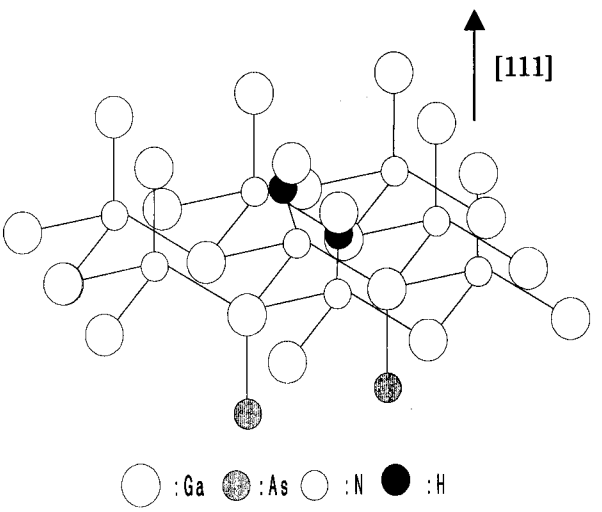

Fig. 4. Proposed microscopic model of the N-H bonds.

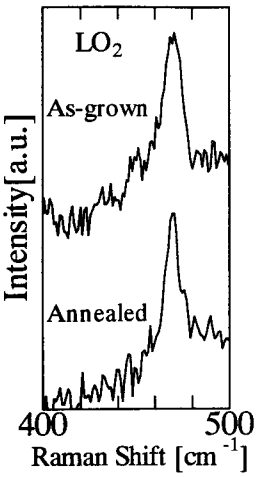

Fig. 5. Typical LO_2 modes from the as-grown and the annealed $GaN_{0.0079}As_{0.9921}$ samples.

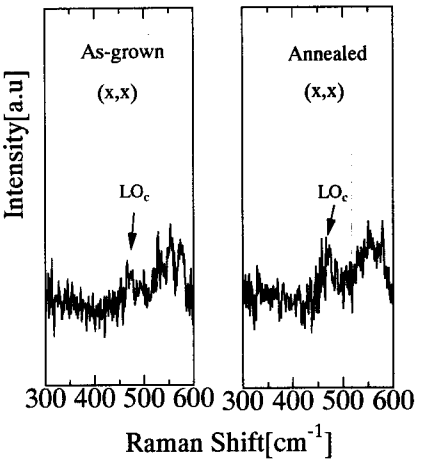

Fig. 7. Typical Raman modes from an as-grown and an annealed $GaN_{0.012}As_{0.988}$ layer in the $z(x,x)\bar{z}$ scattering configuration.

zincblende selection rule due to the change of the crystal symmetry from the T_d one to the $<111>C_{3v}$ one. Furthermore, the frequency of the LOc phonon mode ($257cm^{-1}$) corresponds with the strongly confined GaAs-type phonon modes. Therefore, the Raman results strongly indicate the presence of the trigonal {111}-$(GaN)_1(GaAs)_1$ natural SL clusters in the as-grown GaN_xAs_{1-x} layers.

On the other hand, the FT-IR measurements showed the N-H vibrational mode[1]. In order to keep the symmetry of $<111>C_{3v}$ in the natural SL clusters, the direction of the N-H bonds in the GaN_xAs_{1-x} structures should be required around the <111> directions as shown in Fig. 4.

Figure 5 shows the typical Raman spectra near the LO_2 mode measured in the $z(x,y)\bar{z}$ scattering configuration from the as-grown and the annealed GaN_xAs_{1-x} layers. Any new mode induced by the thermal annealing was not observed in the spectrum from the annealed layer. Therefore, the thermal annealing process basically does not change so much the lattice-structure of the GaN_xAs_{1-x} layers. However, as shown in Fig. 6, the full width of half maximum (FWHM) of the LO_2 modes in the annealed GaN_xAs_{1-x} spectra became slightly narrower than that in the as-grown GaN_xAs_{1-x} spectra. Moreover, the change of the LO_2 mode by the thermal annealing can be seen clearly in the forbidden (x,x) component of the LO_2 mode as shown in Fig. 7. In Fig. 7, the scattering intensity was normalized by the intensity of the TO_1 mode that is strongly enhanced in the GaN_xAs_{1-x} systems. The normalized intensity of the LO_2 mode in the annealed GaN_xAs_{1-x} spectrum clearly

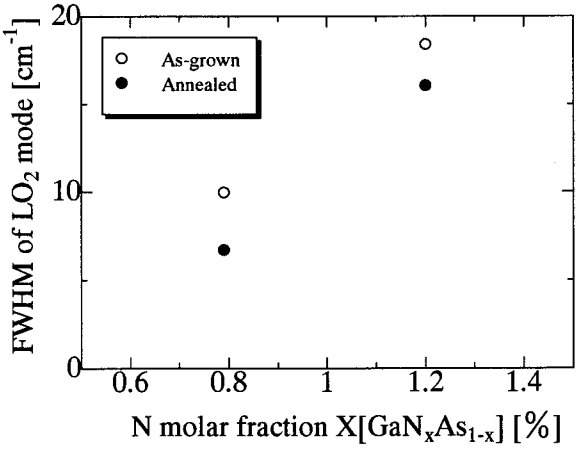

Fig. 6. The FWHM of the LO_2 mode from the as-grown and the annealed layers as a function of N molar fraction.

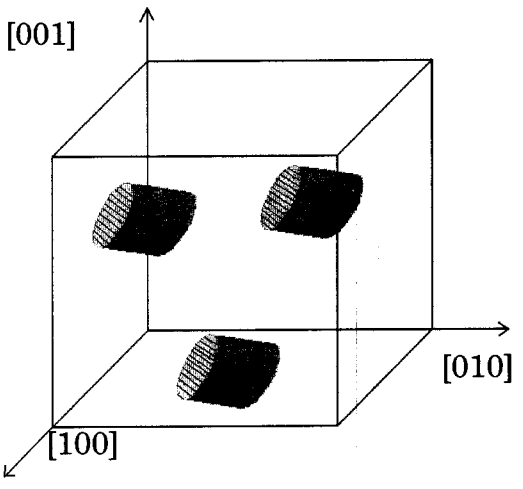

Fig. 8. Schematic illustration of natural superlattice in a GaN_xAs_{1-x} layers.

increased than the case of the as-grown GaN_xAs_{1-x} sample. The result also indicates that the thermal annealing process has an effect to change the locally ordered structures in the GaN_xAs_{1-x} systems.

The FT-IR measurements for the annealed GaN_xAs_{1-x} layers showed that the N-H bonds included in the as-grown GaN_xAs_{1-x} layers were broken by the annealing, and the PL intensity was dramatically increased by the annealing accompanied with breaking of the N-H bonds[1]. Therefore, the Raman results for the annealed GaN_xAs_{1-x} layers indicate that the H-induced degradation in the Ga-N bonds in the trigonal $\{111\}$-$(GaN)_1(GaAs)_1$ natural SL clusters are recovered through breaking of the N-H bonds by the thermal annealing.

4. Conclusions

In conclusions, we have investigated on the Raman scattering from the GaN_xAs_{1-x} layers grown by MOVPE to characterize the locally ordered structure in the GaN_xAs_{1-x} layers. The Raman results indicate that the symmetry is the $<111>C_{3v}$ one in the trigonal $\{111\}$-$(GaN)_1(GaAs)_1$ natural SL clusters as shown in Fig. 8 and, therefore, that the formation of the natural SL clusters occurs during the GaN_xAs_{1-x} growth.

Furthermore, the N-H bonds included in the as-grown layers exist along the $\{111\}$ directions to keep the $<111>C_{3v}$ symmetry. The thermal annealing process for the as-grown layers would be effective for breaking of the N-H bonds and recovering of the Ga-N bonds in the natural SL clusters to improve the crystal quality such as the optical properties.

Acknowledgements

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