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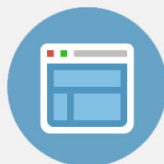
Raman phonon modes of zinc blende In$_x$Ga$_{1-x}$N alloy epitaxial layers

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Transverse-optical (TO) and longitudinal-optical (LO) phonons of zinc blende In$_x$Ga$_{1-x}$N ($0 \leq x \leq 0.31$) layers are observed through first-order micro-Raman scattering experiments. The samples are grown by molecular-beam epitaxy on GaAs (001) substrates, and x-ray diffraction measurements are performed to determine the epilayer alloy composition. Both the TO and LO phonons exhibit a one-mode-type behavior, and their frequencies display a linear dependence on the composition. The Raman data reported here are used to predict the A_1 (TO) and E_1 (TO) phonon frequencies of the hexagonal In$_x$Ga$_{1-x}$N alloy. © *1999 American Institute of Physics.*
[S0003-6951(99)01234-6]

The ternary alloy In$_x$Ga$_{1-x}$N has attracted great attention in the last years due to its successful application in the electronic and optoelectronic device technology. Most of the work has been devoted to the hexagonal phase (h) of the material, the active media in light emitting diodes and laser diodes.[1] In order to understand the device characteristics, the optical properties of h-In$_x$Ga$_{1-x}$N alloy epilayers,[2] double heterostructures,[3] single- and multiquantum well structures[4,5] and quantum dots[6] are investigated. However, very few attempts have been made hitherto to study the zinc blende phase (c) of the alloy despite its potential for practical applications.[7] The electrical transport and structural properties of c-In$_x$Ga$_{1-x}$N ($x = 0.07-1.0$) layers grown by molecular beam epitaxy (MBE) directly on GaAs (001) substrates were reported for the first time by Abernathy *et al* in 1995.[8] Shortly thereafter successful MBE growth of c-In$_x$Ga$_{1-x}$N/GaN epitaxial layers on GaAs (001) substrates exhibiting blue[9] ($x = 0.17$) and green[10] ($x = 0.4$) photoluminescence was reported. First measurements of the optical gain of c-InGaN were also reported recently.[11] Despite the extensive investigations carried out on the hexagonal material and the encouraging first results obtained for its cubic counterpart, even the main mechanisms involved in the luminescence emission from the InGaN mixed crystals remain to be understood.[2,3,6]

In this letter we report on the results of a study of the vibrational properties of zinc blende In$_x$Ga$_{1-x}$N epitaxial films using first-order micro-Raman spectroscopy. The zone center (Γ) transverse-optical (TO) and longitudinal-optical (LO) phonon frequencies are determined for the alloy in three different compositions, $x = 0.07$, 0.19, and 0.31. No Raman data have been published for the c-In$_x$Ga$_{1-x}$N epitaxial layers. Recently, a Raman spectroscopy analysis of h-In$_x$Ga$_{1-x}$N/GaN films was performed, however, the ob-

served peaks in the reported spectrum were ascribed to the first and higher order phonon modes of GaN.[12] The A_1 (LO) and E_2 phonon frequencies of the h-In$_x$Ga$_{1-x}$N alloy with an In content varying between 1.9% and 11.3% were measured by Raman spectroscopy.[13] The LO phonon frequencies measured by us are fairly consistent with these reported data. Based on early infrared reflectivity experiments on h-In$_x$Ga$_{1-x}$N polycrystalline films[14] and recent Raman data for the c-InN and c-GaN binary compounds[15,16] we use our results to predict the A_1 (TO) and E_1 (TO) phonon frequencies of the hexagonal alloy.

The samples analyzed here are grown on GaAs (001) substrates by plasma assisted MBE using a RIBER 32-system equipped with elemental sources of Ga and As and an Oxford Applied Research CARS 25 RF activated plasma source. The N$_2$ background pressure in the growth chamber is of about 5×10^{-3} Pa. Before starting the InGaN growth, a GaN-buffer layer is grown on GaAs at a substrate temperature of about 720 °C using Ga-rich conditions to prevent the formation of the hexagonal phase. For the growth of InGaN the substrate temperature is decreased to 600–670 °C. The flux ratio In/Ga is varied between 100 and 500. The growth process is monitored by reflection high energy electron diffraction (RHEED) and a RHEED-image recording system. The thickness of the GaN buffer and c-InGaN films are of about 100 and 300 nm, respectively.

The alloy composition is obtained from the measured lattice constants (a) through Vegard's law.[14] The values of a are determined by x-ray diffractometry (XRD) with a Philips X Pert High Resolution Diffractometer. Figure 1 depicts the standard $\omega - 2\theta$ XRD scans along the symmetric (002) reflexes of the analyzed samples. The spectra are well fitted by pseudo-Voigt functions leading to the position of two peaks for each sample. The peak at $2\theta = 39.90°$ is the c-GaN reflection corresponding to $a = 4.52$ Å. The peaks at lower values of 2θ are ascribed to the c-In$_x$Ga$_{1-x}$N layers as indicated in Fig. 1. From reciprocal space maps of the symmetric (002) and the asymmetric (113) Bragg reflex we find that our
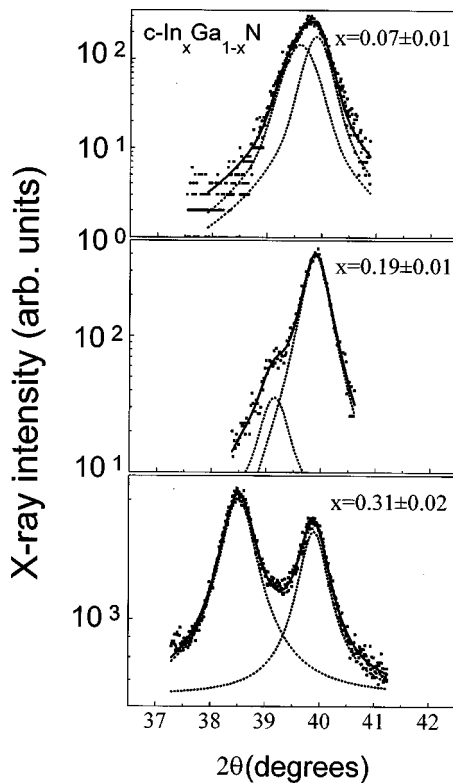
FIG. 1. The (002) Bragg reflex of c-In$_x$Ga$_{1-x}$N epitaxial layers with an alloy composition $x = 0.07$, 0.19, and 0.31. The squares are the experimental results and the solid curves are the least-square fits with two pseudo-Voigt functions for each sample.

FIG. 2. Room-temperature micro-Raman spectra of the c-In$_x$Ga$_{1-x}$N epitaxial layers with $x = 0.07$, 0.19, and 0.31 obtained in this work. The data for c-InN ($x = 1$) and c-GaN ($x = 0$) are taken from Refs. 15 and 16, respectively.

In$_x$Ga$_{1-x}$N layers are fully relaxed. The maximum of the reflected intensity from the In$_x$Ga$_{1-x}$N layer is located along a direction in reciprocal space which connects the origin with the maximum of the GaN Bragg reflex. For the $x = 0.07$ sample relaxation of the lattice was also observed during growth. The distance of RHEED reflexes changed notably revealing a change of the in-plane lattice constant of $\Delta a/a = 0.007 \pm 0.002$. The In content in the samples are determined by interpolating linearly the value of a for c-GaN and that[15,17] for c-InN ($a = 4.97$ Å) as a function of x.

The micro-Raman experiments are carried out at room temperature using a T64000 Jobin–Yvon Raman system with a charge coupled device as a detector. The 488.0 nm line of an argon-ion laser is employed as the excitation and the power is kept below 3 mW. The microscope objective in the setup allows the laser beam to be focused on a spot of about 2 μm. The measurements are made in backscattering from (001) surface. The incident radiation is polarized along the [110] crystallographic direction and no analyzer is used in the scattered light path. The spectral resolution is about 5 cm^{-1}.

Micro-Raman spectra of the c-In$_x$Ga$_{1-x}$N layers with $x = 0.07$, 0.19 and 0.31 are shown in Fig. 2. The spectra for the pure binary compounds c-InN and c-GaN are taken from Refs. 15 and 16, respectively. The evolution of the TO and LO peak frequencies along the alloy composition is indicated by black arrows. The peak frequency at 625 cm^{-1} is tentatively ascribed by us to the LO phonon mode of the alloy with $x = 0.8$. We address this issue later. The facts that the TO and LO phonon frequencies of c-GaN are well known[16]
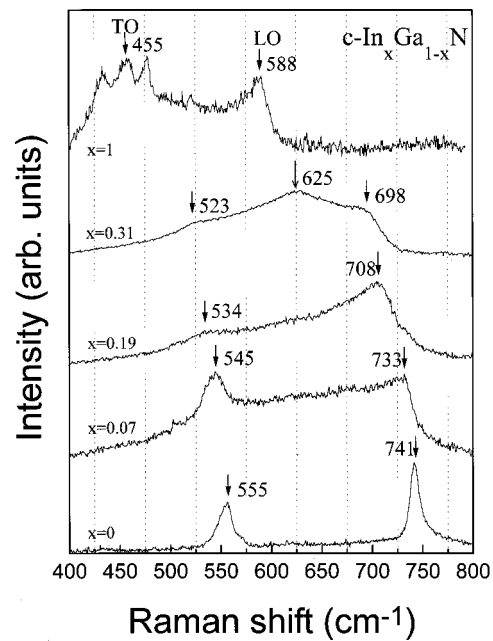
and those of c-InN were recently measured,[15] allow us to make a consistent analysis of the data for the alloy. Figure 3 depicts the phonon frequencies as a function of the In content in the samples. The plot shows that the measured TO and LO phonon frequencies of the alloy lie on straight lines connecting the corresponding values obtained for the c-GaN and c-InN epitaxial layers. The Raman data discussed here lead to the conclusion that the TO and LO phonon modes of c-In$_x$Ga$_{1-x}$N ternary alloy exhibit a one-mode-type behavior. Moreover, their energies depend linearly on the alloy composition.

Let us turn now to the analysis of the phonon peak at 625 cm^{-1} observed in the sample with $x = 0.31$. Reciprocal space maps of the symmetric (002) and the asymmetric (113) Bragg reflex yield clear evidence for a Bragg reflex of an In-rich phase in this sample. The component of the scattering wave vector parallel to the direction of the sample surface (in plane) is approximately equal to the in-plane scattering wave
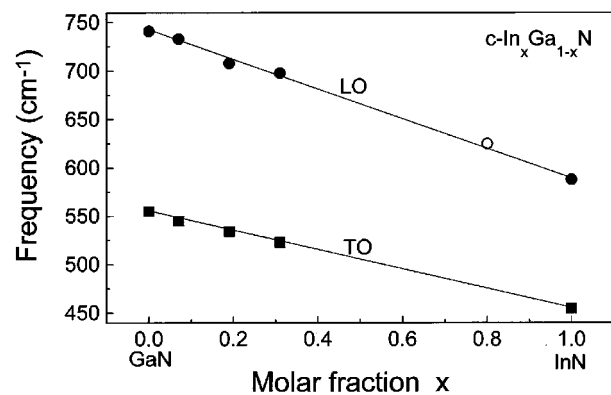

FIG. 3. TO and LO Raman mode frequencies at Γ of the c-In$_x$Ga$_{1-x}$N epitaxial layers as a function of the alloy composition. The straight lines connect the frequencies of the pure binary compounds.

TABLE I. TO phonon frequencies at Γ (cm^{-1}) of the In$_x$Ga$_{1-x}$N alloy. The entries for the cubic systems are from the present Raman measurements and for the hexagonal ones are predictions. The results for the pure GaN ($x=0$) and InN ($x=1$) are from previous Raman experiments.

	Cubic	Hexagonal	
x	TO	A_1 (TO)	E_1 (TO)
0.00	555[a]	537[a]	556[a]
0.07	545	527	554
0.19	534	511	545
0.31	523	495	536
1.00	457[b]	400[c]	490[c]

[a]See Ref. 16.
[b]See Ref. 15.
[c]See Ref. 19.

vector component of the In$_x$Ga$_{1-x}$N ($x=0.31$) layer reflex. Therefore, a tetragonal distortion of the unit cell of the In-rich phase has been taken into account in the calculation of its composition revealing $x=0.80\pm0.05$. We suggest that the $x=0.8$ phase is due to strained In-rich crystalline inclusions which are presumably formed by spinodal decomposition[18] taking place at higher In flux in this sample. Evidence for the phase separation seems to be also present in recently reported XRD spectrum of a c-In$_{0.4}$Ga$_{0.6}$N layer.[10] Therefore, we are tentatively ascribing the peak at 625 cm^{-1} to the LO phonon mode corresponding to the alloy composition $x=0.8$. The white circle in Fig. 3 indicates that this assignment follows the linear trend observed for the data.

Results from infrared reflectivity measurements[14] show that the E_1 (TO) phonon frequencies in h-In$_x$Ga$_{1-x}$N films display a linear dependence on the alloy composition. Raman scattering measurements lead to the E_1 (TO) and A_1 (TO) phonon mode frequencies of h-GaN and h-InN epitaxial layers.[16,19] On the other hand, the frequency (ω) of the TO mode in the cubic and the corresponding frequencies of the A_1 (TO) and E_1 (TO) modes in hexagonal systems are related through the well-known expression

$$\omega_{TO}=[(\omega_{A_1}^2+2\omega_{E_1}^2)/3]^{1/2}. \tag{1}$$

Considering the Raman data reported for h-GaN and h-InN, the linear dependence of ω_{E_1} on the alloy composition and expression (1) we can estimate the TO phonon frequencies of the h-In$_x$Ga$_{1-x}$N alloy. The results are shown in Table I. The entries for the hexagonal alloy are to be taken as predictions to guide further experiments. The results shown in Table I are somewhat different from the recently reported Raman data for h-InN and from theoretical calculations.[20,21] This is expected since the data for the pure binary compound[20] were taken from bulk polycrystalline samples synthesized without a substrate. Moreover, one has to be aware of the fact that the actual reported phonon frequencies of h-InN are quite controversial.[19–23]

In conclusion, good quality c-In$_x$Ga$_{1-x}$N epitaxial layers with x up to 0.31 are successfully grown by MBE. Raman

data are reported for the first time for the c-In$_x$Ga$_{1-x}$N alloy. It is shown that the TO and LO phonon frequencies at Γ for the cubic alloy depend linearly on the In content in the samples and exhibit a characteristic one-mode-type behavior. To guide further experiments predictions are made for the TO-mode (A_1, E_1) frequencies for the h-In$_x$Ga$_{1-x}$N alloy epitaxial layers.

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