Zone-folding effect on optical phonon in GaN/Al_{0.2}Ga_{0.8}N superlattices

C. H. Chen and Y. F. Chen

Department of Physics, National Taiwan University, Taipei, Taiwan, Republic of China

An Shih and S. C. Lee

Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

H. X. Jiang

Department of Physics, Kansas State University, Manhattan, Kansas 6506-2601

(Received 25 September 2000; accepted for publication 3 March 2001)

Optical properties of GaN/Al_{0.2}Ga_{0.8}N superlattices have been investigated by Raman scattering and photoluminescence measurements. It is found that the A₁(LO) phonon decreases in frequency with decreasing quantum-well width. The frequency shift is attributed to the effect of phonon zone folding. Through the study of photoluminescence, we show that our observation of the zone-folding effect on optical phonon in GaN/Al_{0.2}Ga_{0.8}N superlattices is due to the sharpness of the interfaces between barrier and well layers. The sharp interfaces prevent the appearance of mixed interface modes which mask the phonon effect of zone folding in previous reports. © 2001 American Institute of Physics. [DOI: 10.1063/1.1369389]

The group III-nitride wide-band gap semiconductors have been recognized as very important materials for many optoelectronic devices, such as blue UV light emitting diodes (LEDs), laser diodes (LDs), and high-temperature/high-power electronic devices.^{1–3} As demonstrated by LDs, LEDs, and electronic devices, many III-nitride based devices must take advantage of multiple quantum well (MQW) structure such as GaN/Al_xGa_{1–x}N and In_xGa_{1–x}N/GaNMQWs for optimized performance.^{4–6} Therefore, many different optical techniques have been applied to the study of GaN/Al_xGa_{1–x}N MQWs.^{6–8} In addition to the potential application, these QWs are of particular interest for basic investigations, because there the QW consists of binary material and thus no alloy-broadening effects arising from the QW material have to be taken into account. There are few studies⁹ on the use of Raman spectroscopy for the investigation of GaN/Al_xGa_{1–x}N QWs, whereas the experimental technique has been applied successfully to the study of bulk-like GaN^{10,11} and AlGaN¹² layers. In narrow QWs and superlattices, phonon confinement and zone-folding effects can lead to low-frequency shifts of optical phonon modes. In GaN/Al_xGa_{1–x}N material, there is so far no report about such a phonon-frequency shift. In this study, we will provide a demonstration of the zone-folding effect on optical phonon in GaN/Al_xGa_{1–x}N superlattices measured by Raman spectroscopy. Through the photoluminescence measurement, we show that it is the sharp interfaces between the barrier and well layers of the studied samples which enable us to observe the small Raman shift. Our observed frequency shift is in good agreement with the theoretical prediction.

A set of GaN/Al_{0.2}Ga_{0.8}N superlattices with well width $L_w=12, 24$, and $36 \text{ \AA}$ and a fixed barrier width of $50 \text{ \AA}$ has been grown by metalorganic chemical vapor deposition (MOCVD). The GaN/Al_{0.2}Ga_{0.8}N superlattice layers were grown on 0001-oriented sapphire substrate under the optimal GaN-like growth conditions by MOCVD.¹³ The growth temperature and pressure were 1050°C and 300 Torr , respectively. For each of the three samples, prior to the growth of

the superlattices, a $250 \text{ \AA}$ GaN buffer layer and 1 mm undoped GaN epilayer were grown on the sapphire substrate. It was then followed by the growth of the MQW structure with thirty periods of GaN well and Al_{0.2}Ga_{0.8}N barrier. The well and barrier widths were determined by the growth rate of GaN and Al_{0.2}Ga_{0.8}N epilayer under the optimal GaN-like growth conditions. The Raman signal was measured by a DILOR XY800 triple-grating Raman spectrometer. The Raman spectra of the samples were measured at room temperature in vacuum using an Ar laser with a 514.5 nm wavelength. They were measured in backscattering geometry using a micro-Raman setup. The incident and scattered light propagated parallel to the c axis, which in turn was normal to the growth surface. The photoluminescence spectra were recorded by a SPEX 0.85 m double spectrometer, and a photomultiplier tube. The sample was placed inside a closed-cycle He cryostat. A He–Cd laser working at 325 nm was used as the excitation source.

The GaN crystalline in the wurtzite structure belongs to the $C_{6v}^4 (P6_3mc)$ space group. There are two formula units per primitive cell and all the atoms occupy the site of symmetry C_{3v} . Using a conventional group-theory analysis, it can be shown that six optical modes, i.e., $1A_1(\text{TO})+1A_1(\text{LO})+1E_1(\text{TO})+1E_1(\text{LO})+2E_2$, can be observed for the first-order Raman scattering. Figure 1 shows room temperature Raman spectra of three different GaN/Al_{0.2}Ga_{0.8}N superlattice well widths of $12, 24$, and $36 \text{ \AA}$. For these three samples, the GaN E_2 , $E_1(\text{TO})$, $A_1(\text{LO})$, and AlGaN $A_1(\text{LO})$ phonon are observed in the Raman spectra. As shown in Fig. 1, the GaN $A_1(\text{LO})$ phonon is low-frequency shift with well width decreasing, and the other measured phonon modes do not move. Let us now search for the origin of the observed Raman shift. In the superlattice system, strain, optical phonon confinement, and the zone-folding effect are the main effects^{14–18} for the phonon mode shift. If the strain effect dominates the frequency shift, in addition to the A_1 mode, the other phonon modes should be shifted as well, such as GaN E_2 phonon.¹⁹ How-

FIG. 1. Room-temperature Raman spectra of GaN/Al_{0.2}Ga_{0.8}N superlattices with different well widths given in the figure.

ever, this is not the case as shown in our observation. We therefore can rule out the possibility of strain effect. In recent reports,^{20,21} it is known that the phonon density of states of GaN and AlN overlap and there is no gap. The phonon modes of AlGa_N alloys exhibit the so-called one-mode behavior. Therefore, the phonons in GaN/Al_{0.2}Ga_{0.8}N superlattices could propagate through the superlattices, and no optical phonon confinement should occur. We thus believe that the low-frequency shift of A_1 optical phonon is due to the well-known zone-folding effect. In a superlattice system, the artificial structure increases the real space periodicity causing a reduced Brillouin zone. The original phonon dispersion is thus folded into this new zone. States that were originally at $q \neq 0$ values are now at $q = 0$ values. This folding thus results in a redshift of phonon modes and broadening on the low frequency side.^{16–18}

Figure 2 shows the Raman active vibrational eigenvec-

FIG. 2. Raman active optical modes in the wurtzite structure. E_{2l} and E_{2h} correspond to the low- and high-frequency E_2 modes, respectively.

FIG. 3. The measured $A_1(\text{LO})$ phonon frequency in GaN/Al_{0.2}Ga_{0.8}N superlattices. The dot line is the calculated curve from Ref. 22.

tors of four atoms in the unit cell of a wurtzite crystal. The direction of motion can be derived from group theory for all the optical phonons. Concerning the A_1 phonon mode, the direction of motion is parallel to the c axis. However, the other Raman active vibrational modes are perpendicular to the c axis. In the set of our studied samples, the c axis of wurtzite GaN is in the direction of growth. Therefore, the zone-folding only influences the phonon modes in which the motion of atoms has the component along the c axis of wurtzite GaN. This is the reason why the frequency shift occurs only in the A_1 phonon mode, but not in the E_1 or E_2 modes as shown in Fig. 2.

The optical phonon dispersion curve of the A_1 phonon mode can be represented by the expression²²

$$\omega(q) = \omega(0) - \Delta\omega \sin^2\left(\frac{qa}{4}\right), \quad (1)$$

where a is the lattice parameter, q is the phonon wave number, $\omega(0)$ is zone-center phonon frequency, and $\Delta\omega$ is the difference between the zone-center and the zone-boundary frequencies of the phonon dispersion curve of interest. Figure 3 displays the comparison between the experimental and theoretical results for the A_1 phonon mode. The calculated phonon dispersion curve is shown in dot line. As shown in Fig. 3, the experimental points of the peak frequency agree with the calculated curve fairly well. This fact further indicates that the low-frequency shifts can be explained by effect of zone-folding in superlattices.

Figure 4 depicts the photoluminescence (PL) spectrum of the superlattice with well width 36 Å acquired at 15 K. The other PL spectra of 12 and 24 Å are not shown here. The peak at 3.545 eV is attributed to the PL emission from the GaN wells. The linewidth of the emission peaks of these superlattices are 25–32 meV, which is among the narrowest values reported for the GaN/Al_xGa_{1-x}N MQW system. This indicates the interface quality of these MOCVD grown superlattices is reasonably high. Due to the high interface quality, the effects of interface mixing on the frequency shift of phonon modes can be neglected. As shown in the previous report,⁹ the interface-mixing effects will cause a blueshift of the phonon mode, which is in contrast with our observation. An addition evidence of the sharp interfaces of our samples is given by the temperature dependence of the PL measure-

FIG. 4. The photoluminescence from the superlattice with well width 36 Å at 15 K. The peak at 3.565 eV is due to the emission from the GaN wells. The inset shows the temperature dependence of PL peak position of the GaN/Al_{0.2}Ga_{0.8}N superlattices.

ment as shown in Fig. 4. We can see that the PL peak initially increases and then decreases with increasing temperature. A model has been recently proposed to explain the blue temperature-induced shift in InGa_N-based quantum well luminescence.²³ The model is based on band-tail filling of a Gaussian density of state (DOS) with a parameter σ which describes the dispersion of the DOS (i.e., its width). The model calculation is given by²³

$$E(T) = E_D - \frac{\sigma^2}{k_B T}, \quad (2)$$

where E_D is attributed to the energy range between the center of the Gaussian DOS of the electrons and that of the holes. As shown in the inset of Fig. 4, we use this model to analyze our data in order to estimate the extent of the DOS in the superlattice. We obtain the value for σ to be 3–7 meV, which is a relatively small compared to the value of the superlattice emission indicating the high quality of the superlattice interfaces. Indeed, these values correspond to the fluctuations less than an atomic layer. Therefore, we could observe the phonon zone-folding effect in GaN/Al_{0.2}Ga_{0.8}N superlattice layers and the cation intermixing effect at the interfaces can be neglected.⁹ A more detailed PL mechanism will be addressed at a later study.

To conclude, the investigation of Raman scattering carried out on GaN/Al_{0.2}Ga_{0.8}N superlattices has revealed the evidence for phonon zone-folding effect. We provide the PL

measurement to show that our samples have an excellent quality of superlattice interfaces, which prevents the occurrence of the interface mixing effect. Finally, we show that the measured frequency shifts agree with the calculated dispersion curve fairly well. Our measurement therefore provides a demonstration of the phonon zone-folding in GaN/Al_{0.2}Ga_{0.8}N superlattices.

This work was partly supported by the National Science Council of the Republic of China.

- ¹M. A. Khan, A. Bhattarai, J. N. Kuznia, and D. T. Olson, Appl. Phys. Lett. **63**, 1214 (1993).
- ²H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).
- ³S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoko, and Y. Sugimoto, Jpn. J. Appl. Phys., Part 2 **35**, L74 (1996).
- ⁴T. Uenoyama and M. Suzuki, Appl. Phys. Lett. **67**, 2527 (1995).
- ⁵A. Niwa, T. Ohtoshi, and T. Kuroda, Appl. Phys. Lett. **70**, 2159 (1997).
- ⁶H. S. Kim, J. Y. Lin, H. X. Jiang, W. W. Chow, A. Botchkarev, and H. Morkoc, Appl. Phys. Lett. **73**, 3426 (1998).
- ⁷L. Bergman, M. Dutta, M. A. Strosio, S. M. Komirenko, C. J. Eiting, D. J. H. Lambert, H. K. Kwon, and R. D. Dupuis, Appl. Phys. Lett. **76**, 1969 (2000).
- ⁸K. C. Zeng, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **76**, 3040 (2000).
- ⁹D. Behr, R. Niebuhr, J. Wagner, K. H. Bachem, and U. Kaufmann, Appl. Phys. Lett. **70**, 363 (1997).
- ¹⁰M. Giebler, M. Ramsteiner, O. Brandt, H. Yang, and K. H. Ploog, Appl. Phys. Lett. **67**, 733 (1995).
- ¹¹T. Azuhata, T. Sota, K. Suzuki, and S. Nakamura, J. Phys.: Condens. Matter **7**, 129 (1995).
- ¹²K. Hayashi, K. Itoh, N. Sawaki, and I. Akasaki, Solid State Commun. **77**, 115 (1991).
- ¹³K. C. Zeng, J. Li, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **76**, 864 (2000).
- ¹⁴L. Pavesi, G. Mariotto, J. F. Carlin, A. Rudra, and R. Houdre, Solid State Commun. **84**, 705 (1992).
- ¹⁵C. A. Tran, M. Jouanne, J. L. Brebner, and R. A. Masut, J. Appl. Phys. **74**, 4983 (1993).
- ¹⁶B. Jusserand and M. Cardona, *Light Scattering in Solids V* (Springer, Heidelberg, 1989), p. 61.
- ¹⁷G. P. Srivastava, *The Physics of Phonons* (Adam Hilger, Bristol, 1990), p. 263.
- ¹⁸J. Singh, *Physics of Semiconductors and Their Heterostructures* (McGraw-Hill, Singapore, 1993), p. 318.
- ¹⁹J. Gleize, F. Demangeot, J. Frandon, M. A. Renucci, F. Widmann, and B. Daudin, Appl. Phys. Lett. **74**, 703 (1999).
- ²⁰H. Grille and F. Bechstedt, J. Raman Spectrosc. **27**, 201 (1996).
- ²¹C. Bungaro and S. de Gironcoli, Appl. Phys. Lett. **76**, 2101 (2000).
- ²²M. Rajalakshmi and A. K. Arora, Nanostruct. Mater. **11**, 399 (1999).
- ²³P. G. Eliseev, P. Perlin, J. Lee, and M. Osinski, Appl. Phys. Lett. **71**, 569 (1997).