A5.2 Raman and IR reflectance studies of AlGaN

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A INTRODUCTION

Infrared reflection and Raman spectroscopies have been used to derive the energies of the zone center phonon modes in wurtzite Al$_x$Ga$_{1-x}$N ($0 \leq x \leq 1$) [1-5] (for GaN [6] and AlN [7] refer to the dedicated chapters). Selection rules in wurtzite allow a splitting of longitudinal and transversal modes into $A_1$ and $E_1$ modes and the occurrence of additional Raman active modes $E_2$.

B RAMAN SPECTROSCOPY

Phonon frequency

Phonon energies derived in Raman spectroscopy as a function of the determined Al-fraction $x$ in Al$_x$Ga$_{1-x}$N is shown in Fig. 1. $A_1$ modes are marked with triangles, $E_1$ modes with squares, and $E_2$(high) modes with diamond shapes. Results of the different papers are distinguished by different symbol fillings. Fig. 1a) represents an enlarged view of the low composition range in Fig. 1b). Linear interpolations to the original data of the phonon modes are listed in Table 1.

Hayashi et al. [1] have studied phonon modes up to $x=0.15$ in $z(x,x+z)$y right angle scattering and identify $A_1$(TO) (open triangles), $E_1$(TO) (open squares), $E_2$ (open diamonds) and $E_1$(LO) (open squares) modes. Samples were grown in MOVPE with an AlGaN layer thickness of 2-12 µm using a 50 nm AlN buffer layer on (0001) sapphire. Composition was determined by help of x-ray diffraction. A continuous increase of the mode energy with $x$ was observed. An Al$_x$Ga$_{1-x}$N/GaN/sapphire heterostructure grown with AlN buffer layer technique was studied in infrared reflection and Raman spectroscopy by Wetzel et al. [2] (Fig. 2). From an x-ray analysis of the $c$-axis an AlN-fraction of $x=0.15$ was derived. Recently, however, it was shown that AlN-layers in heterostructures with GaN are coherently strained up to a thickness of at least 350 nm. This leads to misinterpretation of the AlN fraction [8]. Including the deformation of the unit cell in the pseudomorphic structure above a value 50% smaller is concluded ($x=0.08$). In backscattering off the $c$-plane the $A_1$(LO) mode was determined at 752 cm$^{-1}$ (square with cross symbol) in excellent agreement with the infrared reflection data [2].

Behr et al. [3] have studied thick bulk-like Al$_x$Ga$_{1-x}$N layers $0 \leq x \leq 0.15$ where $x$ was determined from SIMS and energy dispersive x-ray (EDX) analysis. For the $A_1$(LO) mode a linear increase with $x$ starting at 735 cm$^{-1}$ for GaN is found (triangles with crosses in Fig. 1). Their study also includes a phonon analysis of GaN quantum wells in AlGaN barrier layers.

Cros et al. [5] studied 1 µm Al$_x$Ga$_{1-x}$N ($0 \leq x \leq 1$) layers grown by plasma enhanced MBE on sapphire. The alloy composition was determined by elastic recoil detection analysis and x-ray diffraction. An error margin of 5% absolute was given. For reference AlN from MOVPE was studied. In backscattering of the $c$-plane $A_1$(TO) (filled triangles), $E_2$ (filled and crossed diamonds), and $A_1$(LO) modes (filled triangles) for some ten composition values are obtained. For the $A_1$(TO) branch a linear increase is found with $x$ showing a change of slope at around $x=0.65$. For the $A_1$(LO) mode an upward shift compared to a linear interpolation is found. See Table 1. for an interpolation.

In this study a switching of the $E_2$ mode intensity at around $x=0.5$ by some 50 cm$^{-1}$ to a higher mode energy is observed. Such a two-mode behavior in the mixed crystal of AlGaN differentiates a GaN-like $E_2$ mode and an AlN-like $E_2$ mode. In this study the other modes are found to behave as a direct interpolation of the modes in the binary compounds (one-mode behavior).
Grille and Bechstedt [9] performed calculations of the phonon modes for zincblende AlGaN superlattices within a rigid ion model. In a three-parameter Keating model elastic forces are characterized including the electric forces. The authors predict a two-mode behavior of the TO modes, but a one mode behavior of the LO modes. Through symmetry arguments the wurtzite situation can be connected to the zincblende case and Cros et al. inferred such a two-mode behavior for E\(_2\) as well. In the above experiment, however, a two-mode behavior could not be found for A\(_1\) (TO) but was predicted by theory.

Phonon line width
An analysis of the linewidth of the E\(_2\) phonon modes in Al\(_x\)Ga\(_{1-x}\)N considering samples of \(x\in\{0, 0.06, 0.12, 0.22, 0.70, 1\}\) has been performed by Bergman et al. [4]. Ternary samples were grown by MOCVD on 6H-SiC including a 100 nm AlN buffer. Composition was determined by Rutherford backscattering, EDX, and Auger spectroscopy. Several line broadening mechanisms were considered: contributions of forbidden modes, electron scattering and limited spatial correlation in an alloy. All but the latter could be excluded from the fact that spectra at room temperature and 10 K very essentially identical, no forbidden phonon modes lie close and the fact that as a nonpolar mode E\(_2\) does not couple to electrons. In the framework of the limited spatial correlation of the coherency volumina significant long-range disorder in the ternary alloy was concluded. The maximum linewidth of 20 cm\(^{-1}\) was interpolated at \(x=0.5\). In this work no details are given considering a one- or two-mode behavior of E\(_2\). The modeled data is in excellent agreement with the observed linewidth of the E\(_2\) modes reported by Cros et al. [5] considering the narrower one of both GaN- and AlN-like modes.

C INFRARED SPECTROSCOPY
Phonon modes in an Al\(_x\)Ga\(_{1-x}\)N/GaN/sapphire (\(x=0.15\) neglecting stress, \(x=0.08\) considering stress, see above) heterostructure grown with AlN buffer layer technique was studied in infrared reflection and Raman spectroscopy by Wetzel et al. [2] (Fig. 2).

Figure 1 Raman phonon modes in Al\(_x\)Ga\(_{1-x}\)N versus alloy composition. Symbols represent symmetry of the modes, symbol fillings the original papers. a) is an enlargement of the low composition range in b).
Table 1 Phonon modes in Al$_x$Ga$_{1-x}$N and their linear interpolation. For error margins refer to original references.

<table>
<thead>
<tr>
<th>Phonon</th>
<th>Reference</th>
<th>Interpolation</th>
<th>Comp.Range $(0&lt;x&lt;1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1$(LO)</td>
<td>B</td>
<td>736.4 + 247.4 x</td>
<td>x ≤ 0.15</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>736.5 + 268.3 x - 125.1 x$^2$</td>
<td>x ≤ 1</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>736 + 200 x</td>
<td>x ≤ 0.08</td>
</tr>
<tr>
<td>E$_1$(LO)</td>
<td>H</td>
<td>743.2 + 290 x</td>
<td>x ≤ 0.15</td>
</tr>
<tr>
<td>E$_2$</td>
<td>H</td>
<td>569.7 + 18.8 x</td>
<td>x ≤ 0.15</td>
</tr>
<tr>
<td>GaN-like</td>
<td>C</td>
<td>556.3 + 51.0 x</td>
<td>x ≤ 0.80</td>
</tr>
<tr>
<td>AlN-like</td>
<td>C</td>
<td>620.8 + 47.3 x</td>
<td>x ≥ 0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>= 668.1 + 47.3 (x-1)</td>
<td>x ≥ 0.36</td>
</tr>
<tr>
<td>E$_1$(TO)</td>
<td>H</td>
<td>560.7 + 52.8 x</td>
<td>x ≤ 0.15</td>
</tr>
<tr>
<td>A$_1$(TO)</td>
<td>H</td>
<td>533.6 + 81.3 x</td>
<td>x ≤ 0.15</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>516.0 + 75.0 x</td>
<td>x ≤ 0.64</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>446.8 + 186 x</td>
<td>x &gt; 0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>= 632.8 + 186 (x-1)</td>
<td>x &gt; 0.64</td>
</tr>
</tbody>
</table>

H Hayashi et al. Ref. [1]  
W Wetzel et al. Ref. [2]  
B Behr et al. Ref. [3]  
C Cros et al. Ref. [4]

For light propagating along the c-axis only E$_1$ modes are active in infrared spectroscopy. Transmission is blocked in the Reststrahlenband stretching from the TO to the LO phonon mode. In this multilayer structure infrared reflection is dominated by the Reststrahlenband of sapphire that produces the overall step function with a cut-off near 900 cm$^{-1}$. The reflection of the layered structure was modeled using the bulk properties of the layers and a transfer matrix scheme for layers of arbitrary number and thickness. The simulated spectra are included in Fig. 2 and the individual phonon modes are identified. Due to the thin layered structure on top of the reflecting sapphire selection rules are changed allowing the observation of additional modes (Beeremann effect). The A$_1$(LO) mode in GaN at 736 cm$^{-1}$ appears as a narrow reflection minimum in front of the sapphire signal. Similarly the A$_1$(LO) mode of AlN appears at 887 cm$^{-1}$. The broad minimum is identified as an interference within the nitride layers. The distinct additional minimum at 752 cm$^{-1}$ is identified as the A$_1$(LO) mode in the ternary AlGaN layer. For comparison the respective Raman signal is shown (trace d) showing both A$_1$(LO) modes in GaN and AlGaN. Due to the changed selection rules in infrared reflection both methods provide information on the same phonon modes.

D SUMMARY

Phonon modes in ternary Al$_x$Ga$_{1-x}$N have been determined in Raman and infrared reflection spectroscopy. A two-mode behavior was found for E$_2$(high) with GaN-like and AlN-like branches. Such a behavior had been predicted for TO modes in zincblende material. From an analysis of the E$_2$ linewidth a strong long-range disorder was concluded. In this data little is known about the stress conditions of the material studied. Due to the large critical layer thickness of AlGaN, i.e. on GaN. This may affect the interpretation of the composition from x-ray diffraction and the phonon frequencies themselves. Similarly to GaN coupling to free carriers should affect the infrared active phonon modes. These arguments might explain the discrepancies on the reported A$_1$(TO) and A$_1$(LO) modes as seen in the case of GaN ($x=0$) limit.

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REFERENCES


Figure 2 Reflection a) and Raman spectra d) of Al$_{0.08}$Ga$_{0.92}$N/GaN/sapphire structure. Trace b) gives a magnified portion of a) Simulation is given in c) [b) and c) are offset for clarity] [2].