Chapter 2 Theoretical Backgrounds

2-1 Wurtzite Structure

Group-III nitrides crystallize in cubic structure (zinc-blende) or hexagonal structure (wurtzite). In both structures, a Ga atom is surrounded tetrahedrally by four N atoms for GaN. The zinc-blende and wurtzite structures differ in the stacking order of the lattice with two basis, Ga and N atom. The stacking sequence is ABCABC……in the zinc-blende structure along the cubic [111] direction, while it is ABABAB…… along [0001] direction in the wurtzite structure, as shown in Fig2-1-1. Here A, B, and C denote the site of lattice point.

Since the unit cell length of wurtzite along [0001] doubles that of zinc-blende along [111], the phonon dispersion curves of wurtzite along [0001] ($\Gamma \rightarrow$ A in Brillouin zone) can be deduced by folding those of zinc-blende along [111] ($\Gamma \rightarrow$ L), as shown in Fig2-1-2. By the folding, there are eight sets of phonon normal modes at the Γ point, which is consistent with the prediction of eight irreducible representations in wurtzite structure (C_6^v point group).

$$\Gamma = 2A_1 + 2E_1 + 2B_1 + 2E_2$$

Among them, one A_1 and one E_1 are acoustic modes while B_1 mode is silent for Raman and Infrared processes. Because of the macroscopic electric field anisotropy induced by polar phonons, both A_1 and E_1 split into LO and TO modes. The splitting is not shown in Fig2-1-2. So there are six Raman-active phonons.

The Raman-active modes scattering efficiency is given by:

$$S \alpha \mid \varepsilon_s \bullet \chi \bullet \varepsilon_i \mid^2 .$$

Where ε_i and ε_s denote polarization for the incident and scattered light,
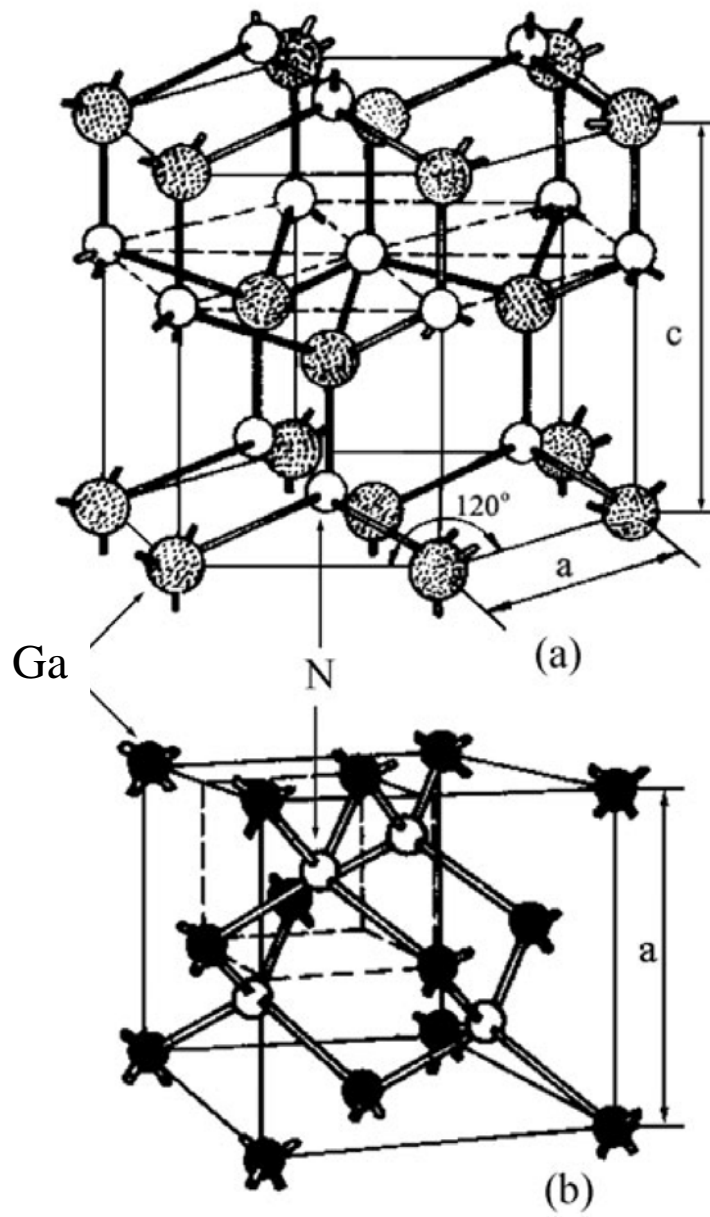
Ga

N

(a)

(b)

Fig.2-1-1 GaN in (a) wurtzite (b) zinc-blende structure

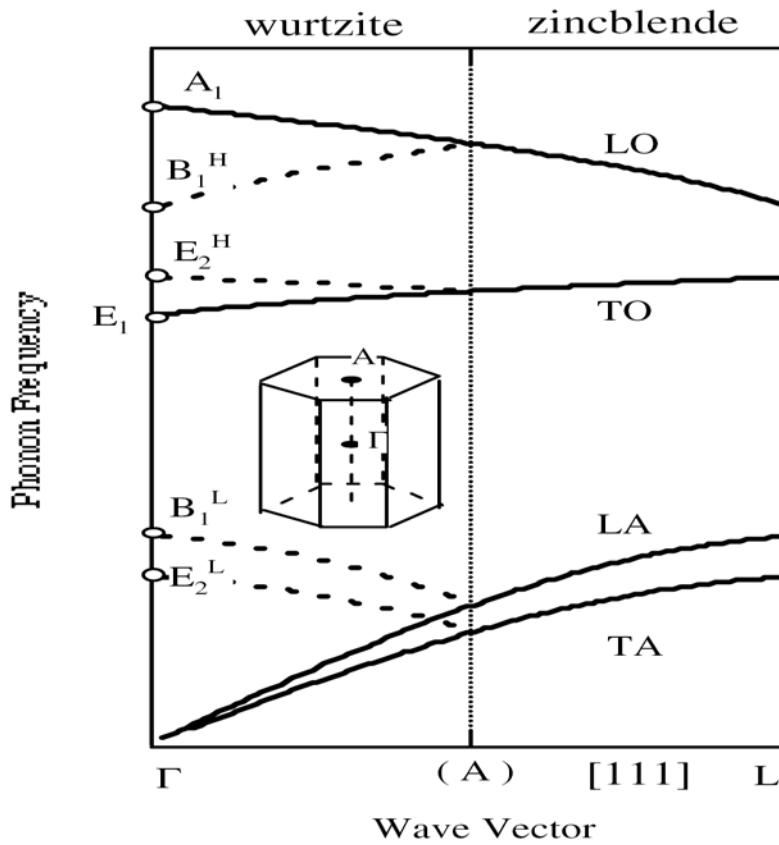Fig.2-1-2 Phonon dispersion relation curves of GaN[10]

Scattering configuration	Allowed modes
$x(y, y)\bar{x}$	A_1(TO)，E_2
$x(z, z)\bar{x}$	A_1(TO)
$x(z, y)\bar{x}$	E_1(TO)
$x(y, z)y$	E_1(TO)，E_1(LO)
$x(y, y)z$	E_2
$z(y, x)\bar{z}$	E_2
$z(y, y)\bar{z}$	A_1(LO)，E_2

Table2-1-1 Selection rules of wurtzite structure

respectively, and χ is the Raman tensor of the scattering process. The Raman tensors for the $C_6{}^v$ point group are as follows:

A_1 mode
$$\begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}$$

E_1 mode
$$\begin{bmatrix} 0 & 0 & c \\ 0 & 0 & 0 \\ c & 0 & 0 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ 0 & c & 0 \end{bmatrix}$$

E_2 mode
$$\begin{bmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0 & -d & 0 \\ -d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

From equations above, it is evident that A_1 phonon mode has only diagonal components, while E_1 mode has only off-diagonal components and E_2 mode has both diagonal and off-diagonal components. This means that the A_1 mode can be observed when the incident and scattered light have parallel polarization, while the E_1 mode is observed only in crossed polarization geometry, as shown in Table2-1-1.

2-2 Phonon Properties and Raman Process

The process of incident photons scattered inelastically by optical phonons is called the Raman scattering, which was first discovered by Sir C. V. Raman[8]. The first-order Raman effect involves an incident photon and a scattered photon after creating or annihilating a phonon. The process is similar to the inelastic scattering of X-ray and neutrons. All these processes must obey the energy and momentum conservation laws:

$$\hbar\omega_s = \hbar\omega_i \pm \hbar\Omega$$
$$\vec{k_s} = \vec{k_i} \pm \vec{K}$$

where ω_i and k_i are the incident photon's frequency and wavevector; ω_s, k_s refer to the scattered photon; and Ω, K refer to the phonon created or destroyed in the scattering process, respectively.

The Raman effect depends on the electronic polarizability α which can be expressed as a power series with respect to the phonon amplitude q,

$$\alpha = \alpha_0 + \frac{\partial\alpha}{\partial q}q + ...$$

If $q(t)=q_0\cos\Omega t$ and the incident electric field is $E(t)=E_0\cos\omega_i t$, then the induced electric dipole moment P is given by

$$P = \alpha E = \alpha_0 E_0 \cos\omega_i t + \frac{1}{2}\frac{d\alpha}{dq}\alpha_0 E_0 (\cos(\omega_i + \Omega)t + \cos(\omega_i - \Omega)t) + ...$$

The photons at frequency ω_i are defined as the Rayleigh scattering, where those emitted at $\omega_i + \Omega$ and $\omega_i - \Omega$ are accompanied by absorption or emission of a phonon of frequency Ω. The photons at $\omega_i - \Omega$ give rise to the Stokes line and

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those at $\omega_i + \Omega$ to the anti-Stokes line.

Energy transfer between the scattering system and the incident radiation was introduced to explain the origin of the scattering effect as shown in the diagram of Fig.2-2-1. When a system interacts with radiation energy ν_0, which is far enough below the energy of the band gap and resonance effect can be neglected, electrons are excited to a virtual state and transmit to real states below it immediately. The situation that the electrons at the E_1 state are pumped to the virtual state and relax back to E_1 the state, with no extra energy involved, is the typical Rayleigh scattering. The process in which an electron at E_1 finally relaxes to a higher energy state E_2, by losing some energy while creating a phonon through virtual states, is called Stoke scattering. Similarly, the process of an electron transmits from E_2 to E_1 state by annihilating a phonon and absorbing energy is called the anti-Stoke scattering. The energy difference ΔE between E_1 and E_2 is exactly the phonon energy $\hbar\Omega$.
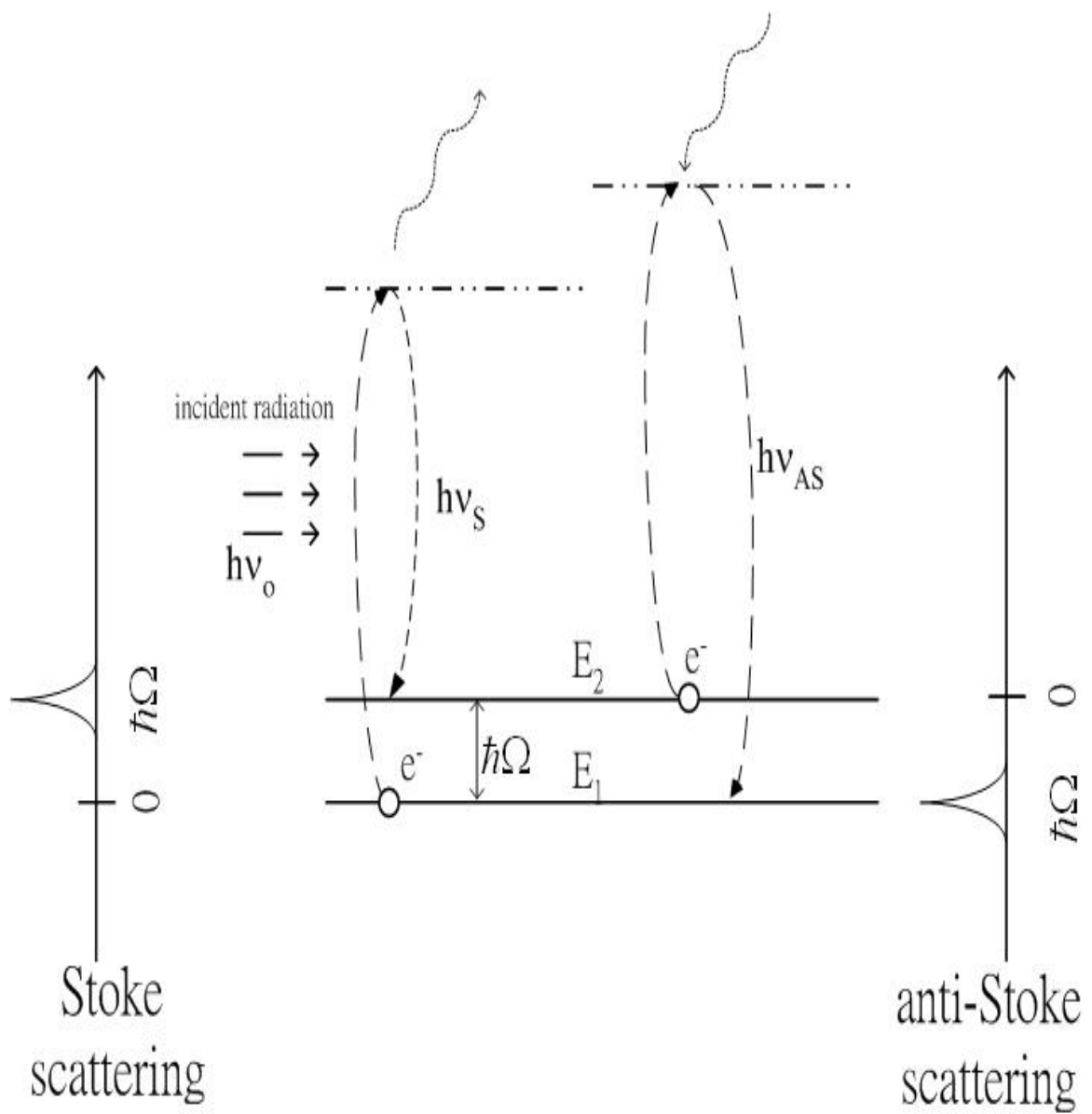
Fig.2-2-1　Diagram of Stoke and anti-Stoke Raman scattering

2-3 LO Phonon - Plasmon Coupling

Electronic excitation due to free charges inside wurtzite GaN can be studied by means of Raman scattering. When the frequency of free carrier plasma oscillation in GaN is close to that of the longitudinal optical (LO) phonon, these two excitations interact via the macroscopic electric fields. The resulting coupled modes can be observed in Raman spectra and their shapes depend on the plasmon damping due to scattering of carriers.

The coupling effect of LO phonon and plasma occurs by means of three mechanisms[9]：(1) deformation-potential mechanism, a modulation of the optical polarizability by atomic displacements；(2) electro-optic mechanism, a modulation of the polarizability by the macroscopic longitudinal field；(3) density mechanism, a direct scattering by electronic-charge-density fluctuations. By combining the three mechanisms, the frequencies of the LO phonon plasmon coupling modes (LOPC), including upper- and lower-frequency branches, can be calculated against the carrier density n. The results from theoretical calculation and experimental data for Si-doped wurtzite GaN in previous studies are shown in Fig.2-3-1. The dashed lines labelled ω_L and ω_T denote the A_1(LO) and A_1(TO) mode without coupling effect, where the dot line ω_p denotes the plasmon frequency. It shows that the upper branch (L^+) appears for carrier density in the order 10^{17}cm^{-3}, and the lower branch (L^-) appears only for higher carrier density ($>10^{18}$cm^{-3}).
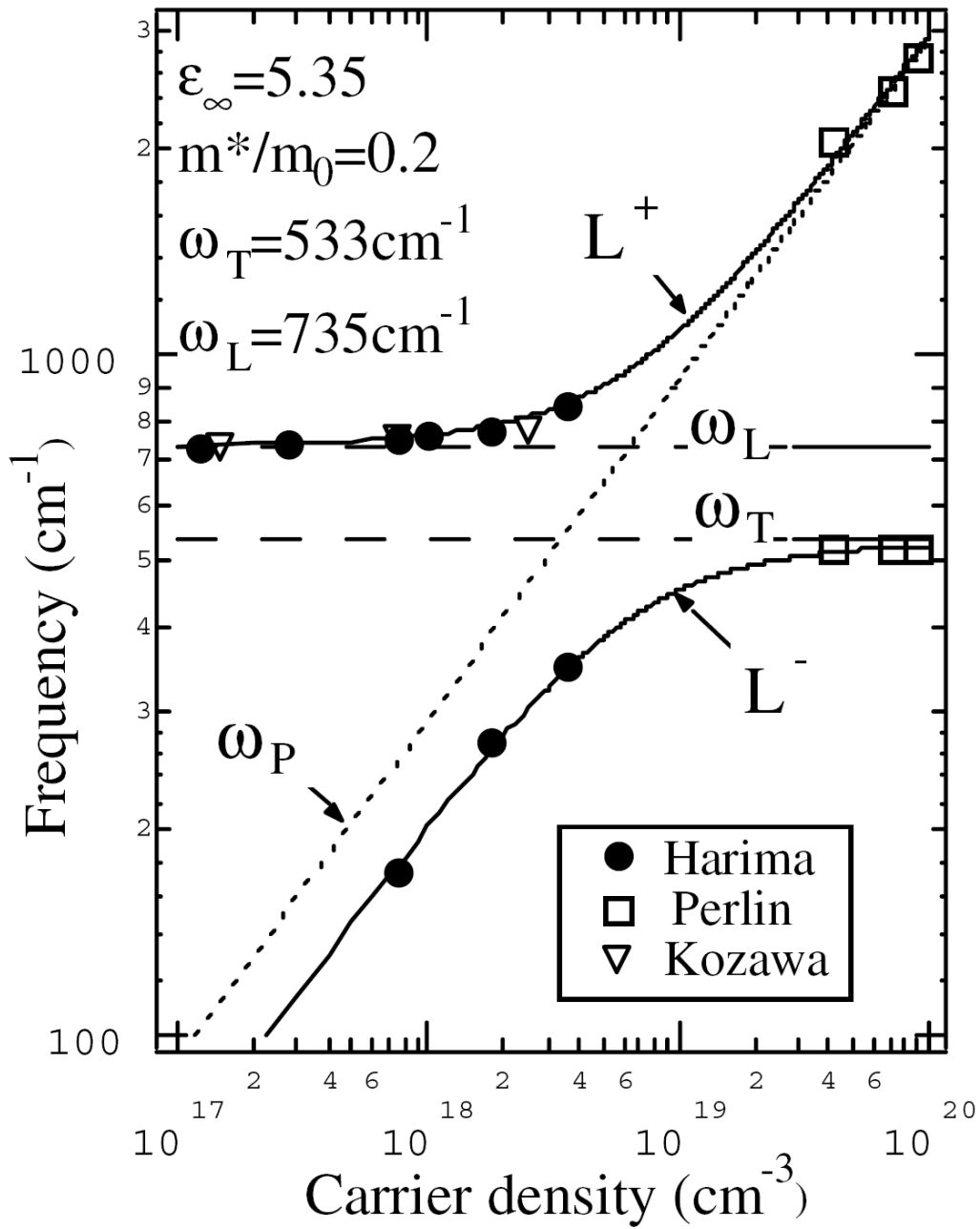
Fig.2-3-1 Theoretical calculation and experimental data for Si-doped wurtzite

GaN[10]