OPTICAL PHONONS IN CUBIC $Al_xGa_{1-x}N$ APPROACHED BY THE MODIFIED RANDOM ELEMENT ISODISPLACEMENT MODEL

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Abstract:

The behaviour of longitudinal and transverse optical phonons in cubic $Al_xGa_{1-x}N$ are derived theoretically as a function of the concentration x ($0 \le x \le 1$). The calculation is based on a Modified Random Element Isodisplacement model which considers the interactions from the nearest neighbor and second neighbor atoms. We find one-mode behavior in $Al_xGa_{1-x}N$ where the phonon frequency in general varies continuously and approximately linearly with x.

Keywords: optical phonons, MREI model, one-mode behavior, $Al_xGa_{1-x}N$.

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1. INTRODUCTION

Much theoretical and experimental effort has been expended in order to understand the fundamental properties of ternary alloys of tetrahedrally coordinated III-nitrides. The motivation comes from their promising applications in optoelectronic heterostructure devices such as LEDs and semiconductor lasers operating from the blue to the ultraviolet (UV) band [1][2]. Ternary alloys of $Al_xGa_{1-x}N$ possess a variable band gaps which can be continuously fine tuned from 3.4eV (GaN) to 6.2eV (AlN) by varying the concentration x [3]. However, studies of III-nitride alloys are complicated because of the shortage of high quality single crystals. For example, there is always structural disorder in $Al_xGa_{1-x}N$, and the growth of high quality single crystal films of $Al_xGa_{1-x}N$ with $0.4<x<0.7$ is still challenging materials researchers.

The complexity involved in the structural and chemical disorder makes ab-initio study of $Al_xGa_{1-x}N$ impractical, and therefore a phenomenological theoretical approach is preferred. The Modified Random Element Isodisplacement (MREI) model, developed by Chang and Mitra [4] and modified by Genzel et al [5] for ternary mixed cubic symmetry crystals, has been successfully applied in II-VI alloys such as $Zn_xMn_{1-x}Te$ [6], $Zn_xMn_{1-x}Se$ [7], and $Zn_xCd_{1-x}Se$ [8]. Reports of experimental Raman scattering in hexagonal $Al_xGa_{1-x}N$ have appeared in the literature [9]-[13], which seem to show that the frequencies of both the A_1 and E_1 polar Raman modes increase smoothly and continuously with increasing x, indicating a one-mode behavior. However, not all of the experimental results are consistent with each other, especially for the E_2 mode, which is probably attributable to significant differences in the quality of the samples used by different researchers. To the best of our knowledge, a

theoretical approach to the concentration dependence of the Raman modes has not yet been developed.

Although the stable structure of $Al_xGa_{1-x}N$ is hexagonal wurtzite like GaN and AlN, Verleur and Barker [14] have showed that the local field in the hexagonal wurtzite structure differs by only 5% with respect to the corresponding one in the cubic zinc-blende structure. Zinc-blende GaN has been experimentally realized [15], it is expected that zinc-blende nitride will be more amendable to doping into n-type or p-type than wurtzite ones. Therefore it is meaningful to characterize theoretically the properties of the zinc-blende nitride. In this paper, we approach the optical phonon behavior of cubic $Al_xGa_{1-x}N$ using a Modified Random Element Isodiaplacement (MREI) model, and reveal the concentration dependence of the phonon frequencies.

2. MREI MODEL

The fundamental assumptions of the Random Element Isodisplacement (REI) model are that in the long-wavelength limit at the zone center (i.e., at q~0), the anions and the cations of vibrate with the same phase and amplitude, and the force which each ion experiences is provided by a statistical average of the interaction with its neighbours. To take into account the second neighbour effect, Genzel et al [5] and Peterson et al [6] introduced a modification with the emphasis on the use of the local fields and a complete determination of the concentration dependence of their phonon frequencies by the macroscopic parameters of the pure end materials. The MREI model allows the incorporation of second-neighbor force constants and a linear dependence of the force constants on the lattice parameter into the model without

resorting to microscopic fitting parameters. Applying the MREI model to $Al_xGa_{1-x}N$, we make two assumptions. The first is the existence of two sublattices: one consists solely of N atoms, and the other one consists of Ga and Al atoms in a random distribution. No short range order is imposed to the distribution of chemical species in the Ga, Al sublattice. The second assumption is that the anions (N) as well as cations (Ga, Al) of the same chemical species vibrate with the same phase and amplitude.

The random condition assumes that each atom is subjected to forces that are the statistical average of interactions with its near neighbors. We take the interactions up to the second neighbor assuming harmonic vibrations. The MREI model also incorporates local electric field effects that depend on the lattice structure.

Taking into account the near neighbor and second-neighbor interactions, the MREI model gives the following equations of motion for N, Ga and Al atoms:

$$
\begin{aligned}
m_N \ddot{\vec{u}}_N &= -(1-x) f_{N\text{-}Ga}(\vec{u}_N - \vec{u}_{Ga}) - x f_{N\text{-}Al}(\vec{u}_N - \vec{u}_{Al}) + e_N \vec{E}_{loc} \\
m_{Ga} \ddot{\vec{u}}_{Ga} &= -f_{Ga\text{-}N}(\vec{u}_{Ga} - \vec{u}_N) - x f_{Ga\text{-}Al}(\vec{u}_{Ga} - \vec{u}_{Al}) - e_{Ga} \vec{E}_{loc} \qquad (1) \\
m_{Al} \ddot{\vec{u}}_{Al} &= -f_{Al\text{-}N}(\vec{u}_{Al} - \vec{u}_N) - (1-x) f_{Ga\text{-}Al}(\vec{u}_{Al} - \vec{u}_{Ga}) - e_{Al} \vec{E}_{loc}
\end{aligned}
$$

In these equations, m, u, and e are the atom masses, the isodisplacements of the atoms from their equilibrium position, and the charges of the ions (Ga, Al) and N in the compounds (for Ga, Al ions, the charges are approximately equal to the Szigeti-effective charges in GaN and AlN), respectively; $f_{Ga\text{-}N}$, $f_{Al\text{-}N}$ are the nearest neighbour and $f_{Ga\text{-}Al}$ the second neighbor bond forces.

The bonding forces between Ga-N and Al-N depend on the bond-length, i.e. on the crystal structure. Since the experimental evidence is that extrapolation of the lattice constants of $Al_xGa_{1-x}N$ to x=0 and x=1 yields the values for GaN and AlN [16]

[26] [27], and the lattice parameter of $Al_xGa_{1-x}N$ changes with the concentration x, therefore the bonding forces between atoms in $Al_xGa_{1-x}N$ are expected to exhibit a dependence on concentration x given by f(x)=F[1+Θ*a(x)], where a(x) is the variation of the lattice constant of the alloy with Al concentration x, and F and Θ are constants. We approximate this dependence as linear in the concentration x, thus

$$\frac{f_{Ga-N}}{f_{Ga-N,0}} = \frac{f_{Al-N}}{f_{Al-N,0}} = \frac{f_{Ga-Al}}{f_{Ga-Al,0}} = 1-\theta x \qquad (2)$$

where θ is a constant and $f_{Ga\text{-}N,0}$, $f_{Al\text{-}N,0}$ are force constants related to GaN and AlN only and $f_{Ga\text{-}Al,0}$ is a fitted bonding force. The pure end materials, GaN and AlN, have similar chemical bonding, and hence θ is assumed to be the same for both.

Since the local electric field from the polarization of the atoms surrounding cubic sites is given by the Lorentz relation, the relationship between $\vec{E}_{loc}$ and the electric polarization $\vec{P}$ is:

$$\vec{E}_{loc} = \frac{4\pi}{3}\vec{P} \qquad (3a) \qquad \text{for transverse modes (TO modes)}$$

$$\vec{E}_{loc} = -\frac{8\pi}{3}\vec{P} \qquad (3b) \qquad \text{for longitudinal modes (LO modes)}$$

As demonstrated by Peterson et al [6], the parameters of Equations (1)-(3) are related to macroscopic parameters according to the usual Born-Huang procedure [17]:

$$\vec{P} = (1-x)\left[Ne_{GaN}(\vec{u}_N - \vec{u}_{Ga}) + N(\alpha_N + \alpha_{Ga})\vec{E}_{loc}\right] + x\left[Ne_{AlN}(\vec{u}_N - \vec{u}_{Al}) + N(\alpha_N + \alpha_{Ga})\vec{E}_{loc}\right] \tag{4}$$

Here N is the density of ion pairs and α is the electronic polarizability, respectively.

N and α are related by the Clausius-Mossotti equation:

$$\frac{4}{3}\pi N\alpha = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \tag{5}$$

where ϵ_∞ is the high frequency dielectric constant. It is also assumed that in $Al_xGa_{1-x}N$ the density of ion pairs N and the dielectric constant ϵ depend on x as:

$$\begin{aligned} N &= (1-x)N_{Ga-N} + xN_{Al-N} \\ \epsilon_\infty &= (1-x)\epsilon_\infty(GaN) + x\epsilon_\infty(AlN) \end{aligned} \tag{6}$$

The charge neutrality condition is:

$$e_N = (1-x)e_{Ga} + xe_{Al} \tag{7}$$

In the limit of x=0 and x=1, we have the boundary conditions for the end materials GaN and AlN as follows.

For x = 0 (GaN, i.e. the TO mode), we have:

$$\begin{aligned} &\frac{4}{3}\pi N_{Ga-N}(\alpha_N + \alpha_{Ga}) = \frac{\epsilon_\infty(GaN) - 1}{\epsilon_\infty(GaN) + 2} \\ &f_{Ga-N,0} = \mu_{GaN}\omega_{TO}^2(GaN) \end{aligned} \tag{8a}$$

For x = 1 (AlN, i.e. the TO mode),

$$\begin{aligned} &\frac{4}{3}\pi N_{Al-N}(\alpha_N + \alpha_{Al}) = \frac{\epsilon_\infty(AlN) - 1}{\epsilon_\infty(AlN) + 2} \\ &f_{Al-N,0}(1-\theta) = \mu_{AlN}\omega_{TO}^2(AlN) \end{aligned} \tag{8b}$$

here μ denotes the reduced mass and ω_{TO} the Raman shift frequency of the TO mode.

Bringing the equations (2) –(8) together, the eigen frequencies of Eq.(1) have the form:

$$\omega^2 = A \pm (A^2 - B^2)^{\frac{1}{2}} \qquad (9)$$

where the quantities A, B depend on $f_{Ga\text{-}N,0}$, $f_{Al\text{-}N,0}$, $f_{Ga\text{-}Al,0}$, ϵ_∞, θ, and the concentration x. To calculate the transverse and longitudinal modes, we introduced the parameter $\gamma = 3/4\pi$ for the TO mode and $3/8\pi$ for the LO mode. Therefore, using the macroscopic parameters in the limit at x=0 for GaN and at x=1 for AlN, we can describe the optical phonon behavior of cubic $Al_xGa_{1-x}N$ by Eq (1) to Eq (9). Thus, applying the above calculations to $Al_xGa_{1-x}N$, the TO and LO modes may be deduced simply by changing γ and θ.

3. RESULTS AND DISCUSSIOINS

Since experimental results for the Raman active phonon frequencies are not yet available for cubic GaN and AlN, it is difficult to use the macro parameters of these end materials directly in the MREI approach. However, Raman scattering of hexagonal wurtzite-type GaN and AlN have been extensively studied [18]-[23]. We start theoretically with the phonon frequencies of hexagonal GaN and AlN and calculate the cubic Raman frequencies, as demonstrated by Zi Jian [24] and Kim et al [25]. Similarly, the dielectric constants of cubic GaN and AlN have not reported; so the wurtzite-type values were used. The bonding force constants were modified slightly to take account of possible errors involved. Table 1 shows the fitting parameters and bonding force constants used for the MREI approach. The Raman

modes of cubic GaN and AlN were calculated from the experimental wurtzite-type values [18]-[23]. The resulting second neighbor bonding force, as predicted by MREI, is about one fourth of the nearest neighbor bonding force.

The results for the optical phonon behavior of cubic $Al_xGa_{1-x}N$ are plotted in Figure 1 as a concentration profile. The solid lines are Raman active branches and the dashed lines are acoustical branches. For both the TO and LO Raman branches, the phonon frequency varies continuously with concentration from the frequency of GaN to that of AlN. Although the Raman TO branch and acoustical modes show some evidence of bowing, they are approximately linear with concentration. These results are characteristic of a one-mode type optical phonon behavior for cubic $Al_xGa_{1-x}N$. As illustrated in Figure 1, the MREI model depicts no intermediate mode in cubic $Al_xGa_{1-x}N$, reflecting the similar chemical bonding properties and local electric fields of GaN and AlN. The MREI prediction for cubic $Al_xGa_{1-x}N$ is similar to the optical phonon behavior of most experimental studies of hexagonal wurtzite-type $Al_xGa_{1-x}N$ [9]-[13]. Therefore the MREI method should be effective when applied to hexagonal $Al_xGa_{1-x}N$. However, as the MREI model is built on cubic symmetry crystals, some major modifications need to be taken in account to the local electric field and the crystal anisotropy of hexagonal crystals. For example, the symmetric vibration mode T_2 of the zinc-blende-type structure splits into polarized A_1 and E_1 modes along and perpendicular to the *c*-axis of the wurtzite-type structure. On the other hand, some researchers [28] found that the x-dependence of the Ga-N, Al-N and Ga-Al bond lengths in $Al_xGa_{1-x}N$ does not follow the average linear variation as assumed in the MREI model; they undergo a bond angle distortion rather than a bond length change. All of these factors offer a challenge when developing the MREI method for the hexagonal case of wurtzite $Al_xGa_{1-x}N$.

4. CONCLUSION

The MREI model makes a sound theoretical approach for characterizing the optical phonon behavior of cubic $Al_xGa_{1-x}N$. The longitudinal and transverse optical phonons of cubic $Al_xGa_{1-x}N$, as a function of the concentration x ($0 \leq x \leq 1$), reveal a one-mode behavior in $Al_xGa_{1-x}N$, where the phonon frequency in general varies approximately linearly with concentration.

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Table and caption

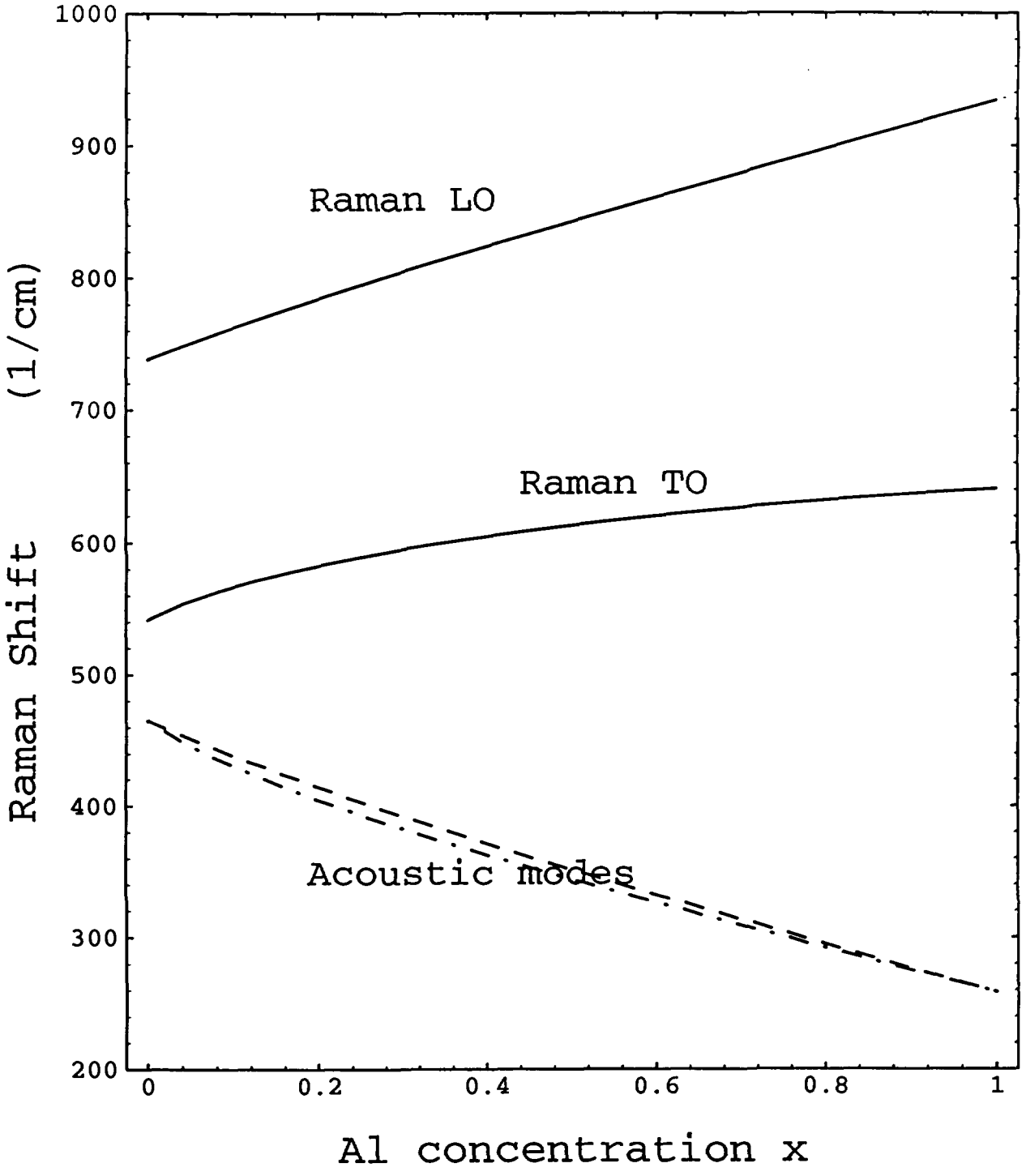
Table 1: Parameters of cubic $Al_xGa_{1-x}N$ used in the MREI model

Raman modes: [a] (cm^{-1})	$\omega_{TO}(GaN) = 552$	$\omega_{TO}(AlN) = 650$
	$\omega_{LO}(GaN) = 742$	$\omega_{LO}(AlN) = 908$
Dielectric constants: [b]	$\epsilon_\infty(GaN) = 5.3$	$\epsilon_\infty(AlN) = 4.84$
	$\epsilon_0(GaN) = 9.5$	$\epsilon_0(AlN) = 8.5$
Lattice constants: [c] (Å)	$a(x) = 4.50\text{-}0.12x$	
Forces constants: (MREI)	$f_{Ga\text{-}N} = 3.95$	
[$\times 10^6$a.m.u.(cm^{-2})]	$f_{Al\text{-}N} = 4.72$	
	$f_{Ga\text{-}Al} = 1.12$	

[a] from Ref: 24, 25
[b] from Ref: 3 references therein.
[c] from Ref:26, 27

Figure caption

Figure 1: Optical phonon behaviour, as a function of concentration x, of cubic $Al_xGa_{1-x}N$


1000
900
800
700
600
500
400
300
200
0
0.2
0.4
0.6
0.8
1
Raman Shift (1/cm)
Al concentration x
Raman LO
Raman TO
Acoustic modes