ISSN 2394-3777 (Print)
ISSN 2394-3785 (Online)
Available online at www.ijartet.com

International Journal of Advanced Research Trends in Engineering and Technology (IJARTET)
Vol. 4, Issue 8, August 2017

# Phonon Properties of various Phases of AlN

Daljit Singh
Dept. of Physics, Ramgarhia College Phagwara

**Abstract**: Group-III nitrides semiconductors are the promising materials for light emitting optoelectronic devices in the blue and green color spectrum and UV region. The large and direct band gap of the group-III nitrides insures that electric field strength of these semiconductors is much larger than that of either GaAs or Si. These semiconductors are also useful for much higher output power delivery in power amplifiers. AlN is a member of group-III nitride family with largest band gap. Along with band gap it also has higher thermal conductivity and is useful at extreme temperature. In spite of considerable technological advancements only reserved effort has been made to study the phonons of AlN. The phonon mode study is important for dynamical, thermo dynamical and other structural properties. Furthermore electron transport and non radiative electron relaxation process depends upon excitations of phonons. So phonon properties are the most desired properties to study. Hence in this study it is decided to study the phonon properties of AlN using de Launey angular force constant model. The results obtained at zone centre are in better agreement with experimental results. The phonon dispersion has been investigated throughout the Brillion zone and hence phonon density of states and variation of specific heat with temperature has been obtained for both phases i.e. cubic and wurtzite phase of AlN.

## I. Introduction

Group-III nitride semiconductors are considered as semiconductors of third generation. The band gap of these semiconductors covers outsized range and can also be tailored by mixing. The large band gap of group-III nitride semiconductors enable these materials of use for optoelectronic devices, light emitting diodes, laser diodes and detectors operating in ultra-violet and visible spectrum. The main features of these materials like short bond length, low compressibility, hardness, high melting point and high thermal conductivity makes them valuable for high frequency and for high power electronic devices at extreme temperature (Fu et al., 2015; Zhang et al., 2013; Bechstedt et al., 2003). AlN a member of group-III nitride family with largest band gap of 6.28 eV (Harima 2002) and it can be of use for light emitting device in UV region. AlN has large bulk modulus, high thermal conductivity and high melting point. The high thermal conductivity enables it suitable for use in microelectronics. Its piezoelectric properties makes it key material for surface acoustic wave sensors and is used to construct piezoelectric micro machined ultrasound transducer, which can collect and send out ultrasound wave and can be used for in-air range findings up to distance of a meter (Prazybyla et al., 2011). Because of the prospective applications of AlN, it is pleasing to study the thermal properties of AlN in detail.

The phonon mode study is important for dynamical, thermal and other important properties. Furthermore vibration of atoms (phonons) also affects the non radiative electron relaxation practice and electron transport (Bungaro et al., 2000. So phonon properties are the most productive properties for these materials. Recently (Fu et al., 2015) and (Zhang et al., 2013) have studied the phonon properties of these semiconductors in wurtzite phase by local density approximation (LDA) and generalized gradient approximation (GGA). The obtained results by both methods mismatches. Recently the phonon properties of these semiconductors were studied theoretically by applying the empirical methods like Keating model rigid ion model, ab initio calculation and valence force model, do not give the physical clarity (Tutuncu et al., 2000; Tutuncu et al., 2002). Therefore in the present study it is decided to study phonon properties such as phonon dispersion curve, phonon density of states and specific heat of AlN has been studied by using de Launey force constant model. As AlN exists in two crystallographic phases cubic and wurtzite phase so phonon properties of both phases has been studied.

## II. Theory

The AlN crystallize in both phases cubic and wurtzite phase. The wurtzite phase has four atoms per unit cell with three acoustical and nine optical modes for a given wave vector while for cubic structure has two atoms per unit cell with three acoustic and three optical modes for a given wave vector. The cubic phase would be favorable as it have higher mobility due to decrease in number of phonons for higher symmetry structure while wurtzite structure is considered as the most stable structure for AlN (Pereira et al., 2003) and also can function at ambient conditions.

All Rights Reserved © 2017 IJARTET

ISSN 2394-3777 (Print)
ISSN 2394-3785 (Online)
Available online at www.ijartet.com

International Journal of Advanced Research Trends in Engineering and Technology (IJARTET)
Vol. 4, Issue 8, August 2017

Therefore phonon properties of both the structure are strongly desired. In this analysis the phonons in the cubic phase and wurtzite phase AlN have been calculated by using de Launey angular force constant model. As this model is used for short range forces and magnitude of the forces generally diminishes after second neighbor, so interatomic interaction upto second nearest neighbor is considered. Short range forces are of two types: central force and angular force. Central force is assumed to be act only along the line joining the mean position of two neighbors and is proportional to relative displacement of the atoms from their equilibrium position and angular forces depend upon the angle which the line joining the atoms makes with the line joining their equilibrium position. The force upto second nearest neighbor are computed separately and then summed up. The separate force constants are used for the central and angular forces. In this study $\alpha_1$ and $\alpha_2$ are the force constants used for central force and $\alpha'_1$ and $\alpha'_2$ are force constants used for angular force for first neighbor and second neighbor respectively.

Now by using DAF model a dynamical matrix of (6x6) has been established for cubic phase and it is solved at zone centre and (q 0 0). The following relations between force constants, frequency and elastic constants have been obtained and are given below.

$$\frac{4}{3}\left(\alpha_1+2\alpha_1^{'}\right)=\left[\frac{mM}{(2m+M)}\right]\omega_0^2$$

$$aC_{11}=\frac{1}{3}\left(\alpha_1+2\alpha_1^{'}\right)+4\left(\alpha_2+\alpha_2^{'}\right)$$

$$aC_{12}=\frac{1}{3}\left(\alpha_1-4\alpha_1^{'}\right)+2\left(\alpha_2-5\alpha_2^{'}\right)$$

$$aC_{44}=\frac{1}{3}\left(\alpha_1+2\alpha_1^{'}\right)+2\left(\alpha_2+3\alpha_2^{'}\right)-\frac{\left(\left(\alpha_1-\alpha_1^{'}\right)^2\right)}{\left(3\left(\alpha_2+2\alpha_1^{'}\right)\right)}$$

Here m is the mass of Al and M being mass of N, a is the lattice parameter, $C_{11}$, $C_{12}$ and $C_{44}$ are the elastic constants. By using experimental values of the elastic constants as given by (Shervin 1991; Marmalyuk 1998) and zone centre frequency (Huan 2008; Alvesa 2002) the force constant has been calculated and are given in table I.

The matrix of (12x12) is obtained for wurtzite phase and is solved at the zone center to obtain relation between some key vibrational frequencies and force constants and thus obtained relations between force constants and some important vibrational frequencies are as given below.

$$\frac{4}{3}\left(\alpha_1+2\alpha_1^{'}\right)=\frac{m_1m_2}{m_1+m_2}\omega^2_{E_1(TO)}$$

$$\frac{4}{3}\left(\alpha_1+2\alpha_1^{'}\right)+2\left(4\alpha_2+2\alpha_2^{'}\right)=m_2\omega^2_{A_1(TO)}$$

$$4\left(\alpha_2^2+25(\alpha_2^{'})^2+10\alpha_2\alpha_2-\alpha_1^2\right)+\frac{16}{3}\left(\alpha_1+2\alpha_1^{'}\right)\left(\alpha_2+5\alpha_2^{'}+\alpha_1\right)$$

$$-\left(\frac{4}{3}\left(\alpha_1+2\alpha_1^{'}\right)+2\alpha_1+10\alpha_2^{'}\right)\left(m_1+m_2\right)\omega^2_{E_2^h}+m_1m_2\omega^4_{E_2^h}=0$$

$$\alpha_2+5\alpha_2^{'}+\alpha_1^{'}=\frac{m_1}{2}\omega^2_{E_2^l}$$

Here $m_1$ and $m_2$ are the mass of X (Al, Ga, B and In) and N atom respectively. By using the experimental values of the zone centre frequencies, $m_1$ and $m_2$ as the input parameter the above equations are solved to calculate force constants. The force constants thus obtained are given in table I.

TABLE I
CALCULATED FORCE CONSTANTS

| Phase | Force constant ($10^4$ dyne $cm^{-1}$) | | | | Lattice constants (Å) | |
|---|---|---|---|---|---|---|
| | $\alpha_1$ | $\alpha_1'$ | $\alpha_2$ | $\alpha_2'$ | a | c |
| Cubic | 23.78 | 3.225 | 4.335 | 0.55 | 3.62 | - |
| Wurtzite | 19.385 | 5.3716 | 6.3666 | -1.7308 | 2.56 | 4.23 |

To calculate phonon density of states we use Blackman's sampling method in which the matrix is solved at 84 non equivalent points with appropriate statistical weight, which results in the creation of mesh in irreducible section of first BZ and the specific heat at constant volume has been calculated from vibrational spectra using sampling technique.

## III. Results And Discussions

It is clear that the calculated force constant $\alpha_1$ between Al-N (central force of nearest neighbor) is strongest among all other Interatomic interactions followed by $\alpha_2$ between similar atoms (central force of second neighbor) and $\alpha_1'$ between Al-N (angular force of nearest neighbor) and it agree with the fact that inter atomic interaction varies inversely to inter atomic distance. This suggests that the

All Rights Reserved © 2017 IJARTET

ISSN 2394-3777 (Print)
ISSN 2394-3785 (Online)
Available online at www.ijartet.com

International Journal of Advanced Research Trends in Engineering and Technology (IJARTET)
Vol. 4, Issue 8, August 2017

bonding between Al-N is stronger as compared to Al-Al and N-N. The angular forces are also contributing significantly.

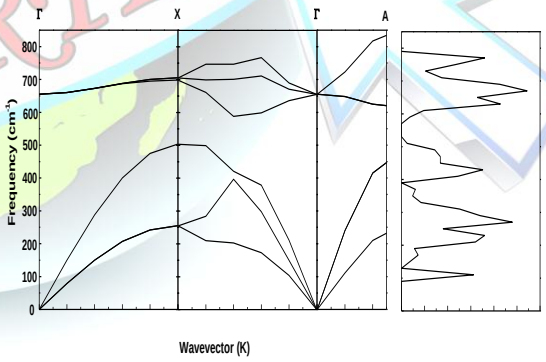
It is also observed that obtained values of $E_1$(TO), $A_1$(TO) and $E_2$ (high) mode show no variation from experimental results while other theoretical results show considerable deviation in case of wurtzite phase. Now dynamical matrix is diagonalized at different points along the symmetry directions [k 0 0], [k k 0] and [k k k]. The plotted phonon dispersion relation indicates that there are two parts in the spectrum, one consists of three acoustical modes for both phases and other consists of nine optical modes for wurtzite phase and three modes for cubic phase but few modes degenerate at the symmetry axis. from the analysis of eigen values of wurtzite phase it is found that the $E_2$ modes (285cm$^{-1}$ and 660 cm$^{-1}$) are Raman active while the $A_1$ (614 cm$^{-1}$) and doubly degenerate $E_1$ (673 cm$^{-1}$) modes are both infrared and Raman active. The $B_1$ modes are (442 cm$^{-1}$ and 673 cm$^{-1}$) are silent. It is observed both tha atoms are contributing to the phonon modes. The nitrogen atom is mainly contributing to the optical modes having higher frequency due to its smaller mass as compared to Al. For $B_1$ (low) mode the contribution of Al atom is negligible while for $B_1$ (high) mode the contribution of N atom is negligible. It is clear from the phonon dispersion curve that upper lying optical modes and $B_1$ mode show slight dispersion while acoustical modes show comparatively additional dispersion. The ratio of masses of cation (Al) and anion (N) originate gap between acoustic and optical branches which can be clearly observed from the phonon dispersion relation. The curve show unusual degeneracy along Γ→A direction. It shows only eight modes in this direction instead of twelve in other symmetry directions, which further reduces to four modes at A point. The similar trends along Γ→A symmetry are also given by others (Fu et al., 2015; Bungaro et al., 2000).

The phonon density of state for wurtzite phase of AlN contains one flattened sharp peaks along with a few small peaks. The sharp peak is observed between 640cm$^{-1}$ to 670cm$^{-1}$ which corresponds to upper lying optical modes which show comparatively lesser dispersion. Whereas small flattened peak at 310 cm$^{-1}$ is due to mixture of acoustical modes and $E_2$ (low) mode and a small sharp peak at 430 cm$^{-1}$ due to flattened $B_1$ (low) mode. While for cubic phase three sharp peaks in optical region along with a number of small peaks in acoustical region. The main sharp peak is observed at about 660cm$^{-1}$ along with slight peaks at 610cm$^{-1}$ and 770cm$^{-1}$, which corresponds to optical modes while peaks observed in acoustical modes are at 110cm$^{-1}$, 290cm$^{-1}$ and 430cm$^{-1}$. The specific heat variation with temperature for AlN for both phases is plotted and is shown in figure 3 and 4.

TABLE II
ZONE CENTRE PHONON FREQUENCIES (CM$^{-1}$) OF AlN

| Phase | Phonon modes | This work | Other theoretical results[a,b] | Other theoretical results[c,d] | Experimental results[e,f] |
|---|---|---|---|---|---|
| Wurtzite | $E_2$(low) | 285 | 233 | 241 | 252 |
| | $B_1$(low) | 442 | 540 | 538 | |
| | $A_1$(TO) | 614 | 597 | 599 | 614 |
| | $E_1$(TO) | 673 | 659 | 655 | 673 |
| | $E_2$(high) | 660 | 638 | 645 | 660 |
| | $B_1$(high) | 673 | 679 | 711 | |
| Cubic | TO | 665 | 660 | 665 | 665 |

a = Zhang et al., (2013), b = Tutuncu et al. 2002,, c = Fu et al., (2015), d = Mohammad et.al 1995, e = Tutuncu et al., (2000), f = Bechstedt et al., 2000

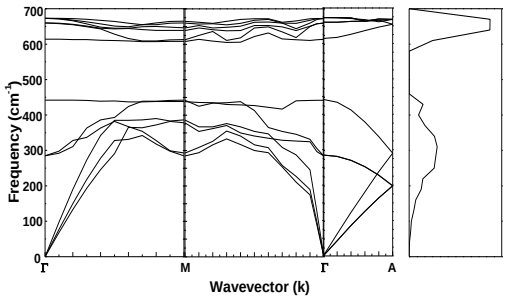



**Graph I Phonon dispersion and phonon density of states of cubic phase**

All Rights Reserved © 2017 IJARTET

ISSN 2394-3777 (Print)
ISSN 2394-3785 (Online)
Available online at www.ijartet.com

International Journal of Advanced Research Trends in Engineering and Technology (IJARTET)
Vol. 4, Issue 8, August 2017




**Graph II Phonon dispersion and phonon density of states of wurtzite phase**

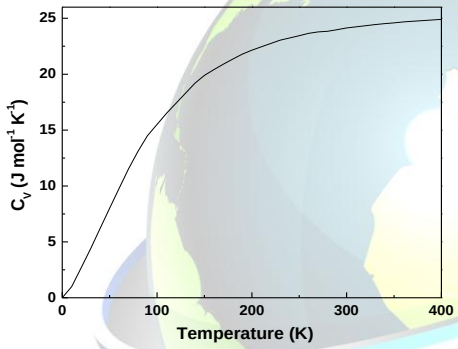



**Figure III Variation of specific heat with temperature of cubic AlN**

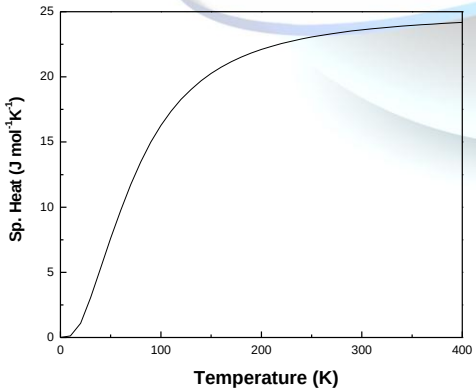



**Figure IV Variation of specific heat with temperature of wurtzite AlN**

## REFERENCES

[1]. Zhang J J, Zhao G J & Liang X X. *First principle studies of phonon III-N compound semiconductors in wurtzite structure*. Int. J. of Appl. Phys. & Maths. 3: 227-230, 2013.

[2]. Fu J. Q., Song T. L., Liang X. X. and Zhao G. J. *First-principle studies of phonons and thermal properties of AlN in wurtzite structure*. J Phys. Conf. ser. 574 012046, 2015.

[3]. Bechstedt F., Furthmuller J. and Wanger J. M. *Electronic and vibrational properties of group-III nitrides: Ab initio studies*. Physica Status Solidi, 6: 1732-1749, 2003.

[4]. Haboeck U., Siegle H., Hoffman A. and Thomsen C. *Lattice dynamics in GaN and AlN with first and second order Raman spectroscopy*. Phys. Stat. Sol. 6: 1710-1731, 2003.Harima H. *Properties of GaN and related compounds studied by means of Raman scattering.* J. of Phys. Condensed Matter 14: 967-993, 2002.

[5]. Przybyla R., Shelton S., Guedes A., Izyumin I., Kline M., Horsley D., and Boser B. In-Air Range finding with an AlN piezoelectric micro machined ultrasound transducer. IEEE Sensors Journal. 11: 2690-2697, 2011.

[6]. Bungaro C., Rapcewicz K. and Bernholo J. Ab initio phonon dispersion of wurtzite AlN, GaN and InN. Phys. Rev. B. 61: 6720-6725, 2000.

[7]. Pandey B. P. and Kumar V. Lattice dynamical and specific heat of ZB III-N. Int. J. Adv. Tech. & Engg. Research. 2 5, 2012.

[8]. Pereira and Srivastva G. P. Origin of the hot phonon effect in group-III nitrides. Phys. Rev. B. 77 155205, 2008.

[9]. Pereira L. S., Santos A. M., Alves J. L. A., Alves H. W. L. and Leite J. R. Dynamical and thermodynamical properties of III-nitrides. Microelectronic J 34: 655-657, 2003.

[10]. Tutuncu H M, bagci S., Shrivastva G.P., albudak A.T. and Ugur G, Structural and dynamical properties of zinc-blende GaN, AlN, BN, and their (110) surfaces. Phys. Rev. B. 71 195309, 2005.

[11]. Tutuncu H. M. and Srivastva G.P. Phonons in zinc-blende and wurtzite phases of GaN, AlN and BN with the adiabatic bond-charge model. Phys. Rev. B 62: 5028-5034, 2000.

[12]. Tutuncu H. M., Srivastva G. P. and Duman S. Lattice dynamics of the zinc-blende and wurtzite phases of nitrides. Physica B. 316-317: 190-194, 2002.

[13]. Mohammad S.N., Salvador A.A., and Morkoc H. Emerging gallium nitride based devices. Proc. IEEE. 83: 1306-1355, 1995.

[14]. Nakamura S. III-V nitride-based light- emitting diodes. Diamond and related materials. 5: 496-500, 1996.

[15]. HuanYou W., Hui Xu, NingDan Z., PengHua Z. The dielectric and dynamical properties of zinc-blende BN, AlN and GaN from first principal calculation. Science of China Series

All Rights Reserved © 2017 IJARTET