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High Temperature Elastic Constant Prediction of Some Group III-Nitrides

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Thermoelastic properties are important for modeling thermal residual stresses and for optimizing the growth conditions of semiconductor thin films. Thermal expansions of AlN and GaN have been evaluated and predicted by us earlier [1] [2]. Here, high temperature elastic constants are estimated empirically from corresponding state relationships and data from other hexagonal Grimm-Sommerfeld compounds. This information together with our earlier thermal expansion data will further improve capabilities for calculating thermal residual stresses in various semiconductor thin films.

1 Introduction and Methods

A material at absolute zero is uniquely represented by the nature of its atoms, their spatial arrangement and the forces between them. In the rigid ion model it is assumed that the electron distribution is locked to the nuclei and is not affected by the lattice dynamics induced by increases in temperature and pressure. As one explores the state of matter at higher temperatures and pressures it is anticipated that most models will have increasing inaccuracies as interatomic interactions responsible for materials behavior are complex, generally non-linear, and are not well understood. Shell representations provide qualitative results for this difficult problem. First principle theories for calculating high temperature elastic constants have many approximations and assumptions and, as indicated earlier [3] [4], have difficulty in reproducing thermal expansion measurements over extended temperature ranges. Calculations of high temperature elastic constants [5] based upon the central force model of Keating [6] [7] also have been questioned on theoretical grounds [8]. Most of the theoretical work provides zero K results for the temperature dependence of assumed quasi-harmonic cubic semiconductors.

It is well known that the thermophysical properties of crystal-chemically similar materials often can be simply correlated by corresponding states relationships [9]. The symmetry of such materials provides a specific mathematical framework for describing the distribution of the fully excited 3N frequencies of a mole of atoms or molecules of a specific crystal structure. The stronger the material the higher is the temperature range that equivalent vibrational modes become excited. Simple correlations for melting, phase transitions and brittle to ductile transition temperatures have been made earlier [10] [11] [12].

In this work we use Debye temperatures as empirical corresponding states parameters to determine the elastic constants of SiC, AlN, GaN and InN from measured elastic constants of CdS [13]. It is assumed that:

$$\frac{C_{ij}^{A}\left(T^{A}\right)}{C_{ij}^{A}\left(\theta_{D}^{A}\right)} = \frac{C_{ij}^{B}\left(T^{B}\right)}{C_{ij}^{B}\left(\theta_{D}^{B}\right)}$$

Where:

$$T^{A} = T^{B}\,\theta_{D}^{A}/\theta_{D}^{B}$$

for compounds A and B. Li and Bradt [14] have predicted the high temperature elastic constants for 6H α-silicon carbide. Their results are utilized as a test for our predictions.

2 Results

Table 1 lists the experimental literature values of the elastic constants for SiC, GaN, AlN and InN at room temperature. Elastic constants of SiC as measured by several authors [15] [16] [17] are also given in Table 1. Table 2 provides our predictions for 6H-SiC. With the exception of a 13% difference for C_{13} the relative differ-

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ences are significantly less than 7% with respect to Li and Bradt's [14] results. The calculated Young's modulus utilizing the Voigt-Ruess-Hill (VRH) average is within -2.3% at room temperature to +0.27% at 1250^{o}K of Li and Bradt's results. Tables 3 , 4 and 5 provide our predictions for AlN, GaN and InN. The room temperature elastic constant values necessary for our calculations are based upon literature results [18] [19] [20] [21] [22] [23] [24] [25] [26] [27] [28]. The Young's moduli calculated from McNeil et al.'s data [19] for AlN are shown in Figure 1 with existing experimental data [18] [19] [20] [29] [30] [31] [32] [33] [34] [35] [36]. For GaN, the room temperature elastic constants are based on the average of consistent measurements [20] [22] [24] [26] [27]. For InN, theoretical values from Wright [37] are applied in our calculation. Although experimental data exists for InN, GaN results generated by the same authors are not consistent with others [28]. The temperature dependence of the Young's moduli for other compounds investigated are provided in Figure 2.

3 Discussion and Conclusions

A complete set of the elastic constants for important semiconducting nitrides has been calculated over an extended temperature range by utilizing an empirical corresponding state relationship. Values shown for the experimentally measured Young's moduli of AlN of Lubis et al. [30] and Ruh et al. [33] are in reasonable agreement with our calculations. They had some porosity in their polycrystalline samples. At higher temperatures one might expect a brittle to ductile transition to occur. This would cause a reduction in the measured Young's modulus. Unfortunately the mechanical property data available for comparison with our calculations is too limited to determine if such a transition occurs. In any case our results should be useful for estimating relative thermal residual stress variations under different growth conditions.

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FIGURES

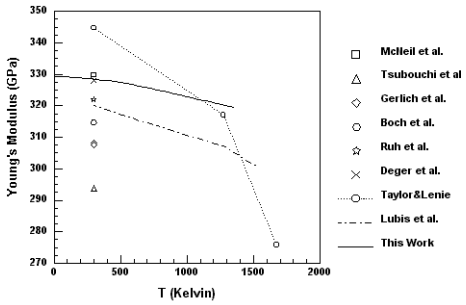

Figure 1. Young's Modulus of AlN

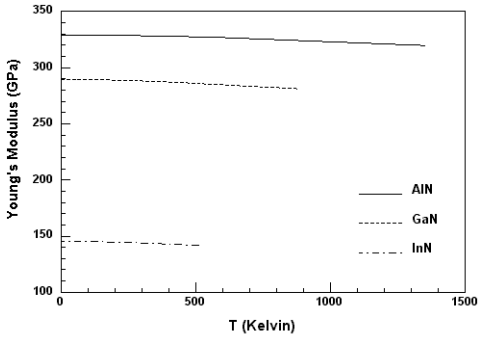

Figure 2. Temperature dependence of Young's Modulus for AlN, GaN and InN.

TABLES

Table 1. Room temperature elastic constants and Debye temperatures for SiC, AlN, GaN and InN.

Compound	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	θ_D (K)	Ref.
GaN	296.0	130.0	158.0	267.0	24.1		[21]
	390.0	145.0	106.0	398.0	105.0		[22]
	374.0	106.0	70.0	379.0	101.0		[23]
	365.0	135.0	114.0	381.0	109.0		[24]
	377.0	160.0	114.0	209.0	81.4		[25]
	370.0	145.0	110.0	390.0	90.0		[20]
	373.0	141.0	80.4	387.0	93.6		[26]
	373.0	141.0	80.0	387.0	94.0		[27]
	374.2	141.4	98.1	388.6	98.3	637.3	*
AlN				404.0			[36]
	345.0	125.0	120.0	395.0	118.0		[18]
	410.5	148.5	98.9	388.5	124.6		[19]
					102.0		[35]
	410.0	140.0	100.0	390.0	120.0		[20]
	424.0	122.0	166.0	353.0	123.0		[34]
	410.5	148.5	98.9	388.5	124.6	965.2	*
InN	190.0	104.0	121.0	182.0	9.9		[28]
	223.0	115.0	92.0	224.0	48.0	375.5	*
SiC	500.0	92.0		564.0	168.0		[15]
	504.0	98.0		566.0	170.0		[15]
				564.9			[17]
	501.0	111.0	52.0	553.0	163.0		[16]
	479.3	98.1	55.8	521.6	148.3	1123.8	*
* Recommended values							

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Table 2. Elastic Properties of 6H-SiC

T (K)	C_{11} (GPa)	C_{33} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{44} (GPa)	E (GPa)
0	469.3	514.3	91.5	48.3	143.8	410.8
50	469.3	514.4	91.5	48.3	143.8	410.8
100	469.3	514.3	91.5	48.3	143.8	410.8
150	469.1	514.1	91.4	48.2	143.7	410.7
200	468.9	513.7	91.4	48.2	143.7	410.6
250	468.6	513.5	91.3	48.2	143.7	410.4
300	468.3	513.1	91.3	48.1	143.7	410.1
400	467.6	512.2	91.1	48.0	143.6	409.6
500	466.8	511.1	90.9	47.8	143.5	409.0
600	465.8	509.5	90.6	47.7	143.3	408.2
700	464.7	508.0	90.4	47.5	143.2	407.4
800	463.4	506.3	90.1	47.3	143.0	406.4
900	461.9	504.6	89.7	47.1	142.8	405.3
1000	460.4	502.9	89.4	46.9	142.6	404.2
1100	458.9	501.2	89.0	46.7	142.5	403.2
1200	457.2	499.6	88.6	46.5	142.3	402.1
1300	455.6	497.9	88.2	46.3	142.1	401.0
1400	454.1	496.2	87.9	46.1	141.9	399.9
1500	452.5	494.5	87.5	45.8	141.7	398.8
1550	451.8	493.6	87.3	45.7	141.7	398.3

Table 3. Elastic Properties of AlN

T (K)	C_{11} (GPa)	C_{33} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{44} (GPa)	E (GPa)
0	411.6	385.5	148.9	99.4	124.1	329.2
50	411.6	385.6	148.9	99.4	124.1	329.2
100	411.5	385.5	148.9	99.3	124.1	329.2
150	411.3	385.2	148.8	99.3	124.1	329.0
200	411.1	385.0	148.7	99.2	124.1	328.9
250	410.7	384.7	148.6	99.0	124.0	328.7
300	410.5	384.3	148.4	98.9	124.0	328.5
400	409.7	383.4	148.1	98.5	123.9	328.0
500	408.7	382.1	147.6	98.1	123.7	327.4
600	407.5	380.8	147.1	97.7	123.6	326.6
700	406.2	379.4	146.6	97.2	123.4	325.8
800	404.7	377.9	145.9	96.7	123.2	324.8
900	403.1	376.4	145.2	96.2	123.0	323.9
1000	401.5	374.9	144.5	95.7	122.9	322.9
1100	399.9	373.4	143.8	95.3	122.7	321.9
1200	398.3	372.0	143.1	94.8	122.5	321.0
1300	396.7	370.5	142.4	94.3	122.3	320.0
1350	396.0	369.8	141.9	94.0	122.3	319.6

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Table 4. Elastic Properties of GaN

T (K)	C_{11}(GPa)	C_{33}(GPa)	C_{12}(GPa)	C_{13}(GPa)	C_{44}(GPa)	E(GPa)
0	376.4	387.1	142.4	99.1	98.5	289.5
50	376.4	387.1	142.4	99.1	98.5	289.5
100	376.1	386.8	142.3	99.0	98.5	289.3
150	375.7	386.5	142.1	98.9	98.5	289.1
200	375.4	385.8	141.9	98.7	98.4	288.9
250	374.8	385.2	141.7	98.4	98.4	288.5
300	374.2	384.4	141.4	98.1	98.3	288.1
400	372.6	382.3	140.6	97.4	98.1	287.2
500	370.7	380.0	139.8	96.7	97.9	286.0
600	368.5	377.8	138.8	96.0	97.7	284.8
700	366.3	375.5	137.7	95.3	97.5	283.5
800	364.1	373.3	136.7	94.5	97.3	282.3
900	362.0	371.1	135.6	93.8	97.1	281.1

Table 5. Elastic Properties of InN

T (K)	C_{11}(GPa)	C_{33}(GPa)	C_{12}(GPa)	C_{13}(GPa)	C_{44}(GPa)	E(GPa)
0	226.7	225.8	117.2	94.4	48.3	145.5
50	226.6	225.7	117.2	94.3	48.3	145.4
100	226.2	225.3	116.9	94.1	48.3	145.3
150	225.7	224.6	116.6	93.6	48.2	145.1
200	225.0	223.7	116.1	93.1	48.2	144.7
250	224.1	222.7	115.6	92.6	48.1	144.3
300	223.1	221.6	115.0	92.0	48.0	143.9
350	222.0	220.5	114.3	91.4	47.9	143.4
400	220.9	219.4	113.5	90.8	47.8	142.9
450	219.7	218.2	112.8	90.2	47.7	142.4
500	218.6	217.1	112.1	89.6	47.6	141.9

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