## Thermodynamics of Boron Arsenide Crystal Growth and

# Characterizations

by

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#### Abstract

Diamond has been known as the best material for conducting heat for decades, but it is scarce, and the synthetic production of diamond is very expensive, slow growth rates, and low quality and has a different thermal expansion rate when it is paired with a semiconductor device. Recently, cubic Boron Arsenide (c-BAs) has represented a new class of high thermal conductivity by both calculations and experimental efforts. Calculation shows the ultrahigh thermal conductivity value of 1400 W m<sup>-1</sup> K<sup>-1</sup> in BAs at room temperature which is the highest thermal conductivity among semiconductor materials.

In this work, BAs single crystal growth with the optimization of chemical vapor transport (CVT) method has been studied and the grown crystals has shown the thermal conductivity value up to 1300 W m<sup>-1</sup> K<sup>-1</sup>. The average lattice constant and density of BAs single crystal was also measured as  $4.79 \pm 0.01$  Å and 5.182 (g cm<sup>-3</sup>), respectively.

Moreover, the reported high thermal conductivity of boron arsenide (BAs) has prompted scientists to characterize the various properties of this material. Thermodynamic data for the enthalpy (H), entropy (S), and Gibbs free energy (G) of BAs were previously predicted from theory. Here, its thermodynamic properties were determined from experimental measurements of its heat capacity (C<sub>p</sub>) over the temperature range of 298 to 1200 K and compared with the predicted data. The thermodynamic properties of BAs at 800 K were calculated to be H = -8.6 kJ mol<sup>-1</sup>, S = 81.0 J mol<sup>-1</sup> K<sup>-1</sup>, and G = -73.4 kJ mol<sup>-1</sup>, and we found that its formation reaction becomes endothermic at 984 K. We also analyzed the experimental findings from growing BAs single crystals (SCs) by the chemical vapor transport (CVT) method. Thermodynamic concepts were applied to show that iodine is the most suitable transport agent among the halogens for obtaining BAs SCs by CVT. Additionally, three different combinations of precursors were employed during BAs SC growth by CVT. The three approaches are described in terms of differences in partial pressure of gaseous species, and their results are compared for possible optimization of the BAs SC growth process by CVT.

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## **Chapter 1** Introduction

A desktop computer needs a fan for cooling but a data center like those in Google or Apple needs a huge water-cooling system and a supercomputer which operates at three petaflops  $(3 \times 10^{15} \text{ operations per sec})$ , for instant, produces the heat which can concurrently warm up couple buildings. With this trend, the next generation of supercomputer (an exaflop machine performing at  $10^{18}$  flops) will consume hundreds of megawatts of power which is equivalent to a small nuclear plant output and that energy would eventually turn to heat (Ball, 2012). With reducing dimensions and increasing power density, thermal management techniques for waste heat treatment is an important area for scientists and engineers in modern micro-electric devices industry to maintain their efficiency sufficiently and expand their lifetime maximally (Waldrop, 2016). The heat flux that today's microprocessors generate is almost comparable to that on the surface of the sun. But to function properly the devices should be cooled to temperatures lower than  $100^{0}$ C, unlike the Sun (Ball, 2012).

Heat can be transferred principally in three ways:

- Conduction
- Convection
- Radiation

But conduction is crucial to efficiently cooling electronic devices due to the compacting units and shrinking dimensions. Thus, high thermal conductivity materials are important for the thermal management of high-power-density electronic devices and have a broad range of applications, such as in microprocessors, smart phones, telecommunication systems, and data centers (Moore & Shi, 2014; Waldrop, 2016).

Those material with thermal conductivity ( $\kappa$ ) exceeding 100 W m<sup>-1</sup> K<sup>-1</sup> at room temperature (RT) is considered high thermal conductivity (Slack, 1973). Metals with high thermal conductivity are the most widely used material in industry. As it was shown in Table 1.1, (Zhong, Liu, Li, & Sun, 2012) Silver (Ag) with thermal conductivity 429 W m<sup>-1</sup> K<sup>-1</sup> and copper (Cu) with 401 W m<sup>-1</sup> K<sup>-1</sup> have the highest thermal conductivity of any metal at room temperature (Incropera, Lavine, Bergman, & DeWitt, 2007). Because of the difficulties and costs of synthesizing, higher thermal conductivity materials are more limited to laboratory researches.

Material	$\kappa (W m^{-1} K^{-1})$		
Lead	34.8		
Tin	67		
Iron	80		
Cast aluminum	163		
Hard aluminum	177		
Pure Al	237		
Au	315 - 317		
Pure Cu	398 - 401		
Ag	411 - 429		

#### Table 1.1. Thermal conductivity of common metal

The heat is carried primarily by free electrons in metals, but it is carried primarily by phonons in non-metals material at room temperature. We are interested in those nonmetal crystals which have a phonon  $\kappa$  at room temperature exceeding that of copper and silver (Slack, 1973). Material possess thermal conductivity exceeding that of copper is defined here as ultrahigh thermal conductivity (Dames, 2018). Table 1-2 shows some common non-metal materials with ultrahigh thermal conductivity (Broido, Lindsay, & Reinecke, 2013; Lucas Lindsay, Broido, & Reinecke, 2013; Tian, Song, Chen, et al., 2018).

Material	$\kappa (W m^{-1} K^{-1})$		
BP	460		
SiC	490		
c-BN	900		
Graphite	2000		
Diamond	2300		

 Table 1.2.
 Some common ultrahigh thermal conductivity materials

Diamond has the highest room-temperature thermal conductivity of 2300 W m<sup>-1</sup> K<sup>-1</sup> and is used as a heat dissipator in electronic devices. However, diamond is scarce, and the synthetic production of diamond is very expensive, slow growth rates, and low quality so it has not been widely used in industry (Dames, 2018; Lucas Lindsay et al., 2013; Qiye Zheng et al., 2018). Graphite also is known to have high  $\kappa$  value of 2000 W m<sup>-1</sup> K<sup>-1</sup> for heat flow perpendicular to the c-axis (along the tightly-bound sheets), but the  $\kappa$  is significantly less for heat flow parallel to the c-axis (Incropera et al., 2007; Slack, 1973). Cubic boron

nitride (c-BN) is difficult to synthesize because it requires high pressures (10 GPa) and temperatures (>2000  $^{0}$ C) (Qiye Zheng et al., 2018). Boron Phosphide (BP) and Silicon Carbide (SiC) are not significantly distinguishable from copper (Tian & Ren, 2018).

Based on the conventional theory, only crystals with light constituent elements like carbon and with strong interatomic covalent bonding should exhibit high lattice thermal conductivity. Based on this theory, the Slack (Slack, 1973) predicted the thermal conductivity of BAs to be 200 W m<sup>-1</sup> K<sup>-1</sup> and for more than 40 years no one questioned or measured this estimation (Dames, 2018).

Recent calculations, however, predicted high thermal conductivity in some cubic boron-V compounds at room temperature, which is an exception from conventional theory (Mori, 2019; Tian, Song, Chen, et al., 2018). Using these calculations, in 2013, Lindsay et al. (Lucas Lindsay et al., 2013) traced these results to fundamental vibration properties which are not connected to this theory for high thermal conductivity in material. Thus, they used quantitative ab initio techniques to predict accurately the  $\kappa$  for the class of boron based cubic III-V compounds. Since the structure of BAs was similar to diamond which has only three-phonon scattering at room temperature, boron arsenide (BAs) was initially predicted to have a room-temperature value of 2200 W m<sup>-1</sup> K<sup>-1</sup> by assuming only three-phonon scattering, similar to thermal conductivity of diamond (Broido et al., 2013; Lucas Lindsay et al., 2013; Zhang et al., 2018). Such a high thermal conductivity is remarkable, although boron (B) is a light element, arsenic (As) is a heavy element (Yue, Xu, & Liao, 2018).

However, a more recent examination considering four-phonon processes predicted a somewhat lower thermal conductivity of 1400 W m<sup>-1</sup> K<sup>-1</sup> at room temperature for BAs which is still triple the value of copper and silver (Feng, Lindsay, & Ruan, 2017; L Lindsay, Hua, Ruan, & Lee, 2018; McGaughey, Jain, Kim, & Fu, 2019; Ravichandran & Broido, 2019). Thermal conductivity measurements of early BAs crystals at room temperature were as high as 350 W m<sup>-1</sup> K<sup>-1</sup>, (Kim et al., 2016; Tian, Song, Lv, et al., 2018; Xing, Glaser, et al., 2018) but our more recent BAs crystal grown have exhibited an impressive thermal conductivity near 1300 W m<sup>-1</sup> K<sup>-1</sup> at room-temperature with TDTR method which is close to the four-phonon theoretical predictions (Kang, Li, Wu, Nguyen, & Hu, 2018; Li *et al.*, 2018; Tian, Song, Chen, *et al.*, 2018). Moreover, growing BAs SC longer than 4 mm makes  $\kappa$  measurement using the steady state (SS) method possible. In this method, a silicon bar is used as reference and is attached to a resistive heater. The BAs sample is attached to reference from one side and to a sink from other side. Using one dimensional Fourier heat transport equation, we calculated the thermal conductivity of BAs by measuring temperature gradient in both BAs and silicon bars (Kraemer & Chen, 2014; Tian & Ren, 2018; Tian, Song, Chen, et al., 2018).

Further research on p-type conductivity of the BAs SC has shown that contaminant elements such as silicon and carbon are prime candidates for reducing the experimental value from the prediction (Chae, Mengle, Heron, & Kioupakis, 2018; Lyons et al., 2018; Wang et al., 2012; Qiang Zheng et al., 2018). Therefore, eliminating these contaminants could be a good strategy for increasing thermal conductivity. However, even the current reported thermal conductivity value of BAs is higher than that of many common high thermal conductivity materials like copper, gold, aluminum, etc. Therefore, the high thermal conductivity of BAs, along with its better mechanical performance than the most used material, silicon, make it a good candidate for future electronic devices (Liu et al., 2018; Tian et al., 2019). Recently, Boron Arsenide has been also confirmed to have an indirect bandgap of 1.7 – 1.8 eV at room temperature which shows that BAs is the only high-thermal conductivity material with semiconducting properties (Bushick, Mengle, Sanders, & Kioupakis, 2019; Gamage, Sun, Ziyaee, Tian, & Ren, 2019; Lyons *et al.*, 2018).

Chemical vapor transport (CVT) has been the only method reported to grow BAs single-crystals (SCs) thus far. Although there has been significant development in growing BAs crystals using this method, challenges remain for the field, including improving the quality and size of the crystals and commercializing the BAs SC growth process (Tian & Ren, 2018). Studying the thermodynamic principles and theory underlying BAs SC growth using the CVT method are primary steps needed to address these challenges. Thermodynamic data for the enthalpy (H), entropy (S), and Gibbs free energy (G) of BAs were previously predicted only from theory because previously they were difficult to obtain by common bulk crystal and thin film growth techniques. Dumont and Monteil (H Dumont & Y Monteil, 2006) in 2006 derived these values for BAs by extrapolation from Aluminum to boron based component based on the analogy of variation and empirical trends of those quantities for several binary series in different III-V compound system like phosphide, nitride, and arsenide by using thermodynamic dataset. However, by improving the crystal growth technics and growing bigger bulk crystal, we were able to calculate these quantities based on the measurement of heat capacity for BAs.

To describe the transport reaction of CVT method quantitatively, we have first quantified the thermodynamic properties of BAs so that the model calculations of the transport reaction can be carried out. Then, by using the calculated thermodynamic data of BAs, we have studied the theoretical concepts underlying the three different approaches to BAs SC growth by the CVT method and compare the theoretical results with the experimental findings (Binnewies, Glaum, Schmidt, & Schmidt, 2012; Ziyaee, Gamage, Sun, Tian, & Ren, 2019).

### **Chapter 2** Boron Arsenide single crystal growth

#### 2.1 Literature review

In 1973, Slack used the theory of the magnitude of  $\kappa$  for nonmetallic crystals in the temperature range  $T \ge \Theta$ , to predict  $\kappa$  of some high thermal conductivity nonmetallic crystals along with BAs. In this theory (Slack, 1973)

$$\kappa = BM_{av}\delta \Theta^3 / T\gamma^2$$
,

where  $\theta$  is the Debye temperature,  $M_{av}$  is the average mass of an atom in crystal,  $\delta^3$  is the average volume of unit cell in crystal, B is a constant, and  $\gamma$  is Gruneisen's parameter (Black, 1972). Based on this theory, commonly accepted criteria for high thermal conductivity nonmetallic crystals include:

- I. Strong interatomic bonding (high  $\Theta$ )
- II. Simple crystal structure (low no. of atom per primitive crystallographic unit cell)
- III. Low atomic mass (high  $\Theta$ )
- IV. Low anharmonicity (small  $\gamma$ )

And gives this rule of thumb that by increasing  $M_{av}$  (consequently decreasing  $\Theta$ ), thermal conductivity decreases because the  $\Theta^3$  term dominates the behavior (Lucas Lindsay *et al.*, 2013). Although this theory matches with most experimental  $\kappa$  values such as diamond, Boron Nitride (BN), Boron Phosphide (BP), Silicon Carbide (SiC), and graphite, it surprisingly suggests  $\kappa$  for BAs of only 200 W m<sup>-1</sup> K<sup>-1</sup> at room temperature.

In 2013, Lindsay *et al.* (Lucas Lindsay *et al.*, 2013) traced these results to fundamental vibration properties which are not connected to this theory for high thermal

conductivity in material. Thus, they used quantitative *ab initio* techniques to predict accurately the  $\kappa$  for the class of boron based cubic III-V compounds. In this first-principles calculation of  $\kappa$ , the atomic vibrations of the lattice given by phonons are considered to be the primarily heat carrier in semiconductors and insulators and is given by

$$\kappa = \frac{1}{V} \sum_{\lambda} C_{\lambda} v_{\lambda\alpha}^2 \tau_{\lambda\alpha},$$

where  $v_{\lambda\alpha}$  and  $\tau_{\lambda\alpha}$  are respectively  $\alpha^{\text{th}}$  velocity component and phonon mean free path (mfp) for a small  $\Delta T$ ,  $C_{\lambda}$  is the specific heat per phonon mode, V is the crystal volume and the sum are over all phonon modes. By considering three-phonons scattering, Lindsay *et al.* were able to predict  $\kappa$  for some high thermal conductivity material as Table 2.1 (Lucas Lindsay *et al.*, 2013). The dominant thermal resistance for optic (o) and acoustic (a) phonons arises with the most important scattering channels including two acoustic phonons combining with one optic (aao), and three acoustic phonons (aaa).

	Mav (amu)	θ(K)	$\kappa (W m^{-1} K^{-1})$	
Diamond	12.01	2280	2290	
c-BN	12.41	2025	940	
BP	20.89	1110	580	
BAs	42.87	700	2240	
BSb	66.28	495	465	

 

 Table 2.1.
 Calculated θ, M<sub>av</sub>, and κ at room temperature of diamond and some Boron - V compounds

Table 2.1 shows that the BAs is second after diamond by attaining an ultrahigh thermal conductivity 2240 W m<sup>-1</sup> K<sup>-1</sup> at RT. The  $\kappa$  also drops from BN to BP by increasing M<sub>av</sub> which match with commonly accepted criteria mentioned above but it has a sharp rise with BAs before drop to BSb. This unusual behavior of BAs is due to

- A large gap of frequency between optic and acoustic phonons (o-a gap) that causes *aao* scattering is prohibited and reduces the thermal resistances in BAs.
- The bunching of the acoustic branches that decreases the phase space.

However, quantitative calculation considering three photon scattering has shown a considerable difference of thermal conductivity comparing to experimental measurement. In 2017, Lindsay and Feng *et al.* (Feng *et al.*, 2017) considered higher-order four-photon scattering from first principles for thermal conductivity calculation which eventually reduced the predicted thermal conductivity of BAs from 2240 W m<sup>-1</sup> K<sup>-1</sup> to 1400 W m<sup>-1</sup> K<sup>-1</sup> at room temperature.

#### 2.2 Growth of BAs single crystal

Chemical vapor transport (CVT) has been the only method reported to grow BAs single-crystals (SCs) thus far. Chu and Hyslop (Chu & Hyslop, 1972) achieved BAs SCs inside a sealed quartz tube for the first time in 1972 but Perri (Perri, La Placa, & Post, 1958) in 1958 was the first one who reported polycrystalline BAs. Recently, multiple groups have made efforts to improve the CVT process to enhance the quality and enlarge the size of crystals (Lv *et al.*, 2015; Tian, Song, Lv, *et al.*, 2018; Xing, Chen, *et al.*, 2018; Xing, Glaser, *et al.*, 2018).

However, due to the danger of the elemental sources and the different chemical properties between B and As, the BAs growth is very challenging. Moreover, reactions above 920 °C would cause the formation of B<sub>12</sub>As<sub>2</sub> which is irreversible and reduces  $\kappa$  significantly. All these challenges have led to slow down research on BAs. Here, BAs SC growth using CVT has been studied based on our lab experiment (Gamage *et al.*, 2019; Tian, Song, Chen, *et al.*, 2018).

Boron bulk particles, arsenic lumps, and iodine powder, with molar ratio of As:I = 20:1 were placed in the quartz tube. Here is the purity of elemental material was used.

B → (Alfa Aesar, 99.9999%)

As → (Alfa Aesar, >99.99999%)

I<sub>2</sub>  $\rightarrow$  (Alfa Aesar, 99.999%)

The quartz tube sealed under vacuum ( $10^{-4}$  Torr) and B particles and I<sub>2</sub> powder were placed at one end (hot end) and As lumps at the other end (cold end) and placed the fused quartz tube in a two zones horizontal tube furnace (Figure 2.1). The hot end of furnace was set at 1163 K and the cold end at 1053 K. The temperature profile has been shown in Figure 2.2 for a growth period of 14 days.

After a growth period of 2 weeks, several millimeters – scale BAs crystals appeared at cold zone. They were carefully picked and washed with *aqua regia* [nitric acid (HNO<sub>3</sub>): hydrochloric acid (HCl) = 1:3]. This process yielded high quality BAs crystals as shown in Figure 2.3. The Scanning Electron Microscope (SEM) image of these crystals has been shown in Figure 2.4.



Figure 2.1. Schematic of chemical vapor transport for BAs SCs growth



Figure 2.2. The temperature profile used in two zones tube furnace to grow BAs SC crystal



Figure 2.3. BAs single crystals grown by CVT method



Figure 2.4. Scanning Electron Microscope (SEM) image of BAs single crystals

# **Chapter 3** Boron Arsenide properties measurement

### 3.1 X-Ray Diffraction

Figure 3.1 shows the powder X-ray diffraction data of BAs using PANalytical machine model X'Pert PRO, with Cu K-α1 and wavelength 1.5406 Å at room temperature.



Figure 3.1. X-ray diffraction of powder BAs at room temperature

To calculate BAs crystal structure, Bragg's law and the expression for the spacing between planes are used as

$$d_{(hkl)} = \frac{\lambda}{2\sin\theta} = \frac{a}{\sqrt{h^2 + k^2 + l^2}},$$
 (3.1.1)



Figure 3.2. Bragg scattering off a plane of atoms in a crystal

where  $\lambda$  is wavelength, a is the lattice constant,  $\theta$  is deflection angle, and *hkl* are Miller's index. Figure 3.2 shows that the excess distance which was traveled by the wave striking the lower plane is  $2d \sin\theta$ . We have also used the expression for the space between planes in a cubic lattice and the lattice constant as

$$a^2/d^2 = h^2 + k^2 + l^2 = N,$$
 (3.1.2)

Table 3.1 shows the calculation parameters. In the first two columns I just read the angles of the peaks in Figure 3.1 and labeled them alphabetically. In the third column I calculated the distance between lattice planes for the given peak using Bragg's law Eq. (3.1.1).

In the fourth column I have calculated the squared ratio of the lattice spacing *d* for the given peak to the lattice spacing for the first peak which is labeled  $d_4$  as a reference. We then realized that these ratios are close to whole numbers divided by 3, so we multiply them by three in the next column which shows that our BAs crystal has Face Centered Cubic (FCC) lattice. In the next column I round these numbers to integers and produce precisely the value of N expected for the FCC lattice. Considering that h, k, l must be all odd or all even for FCC lattice, I found Millor's index in the next column using Eq. (3.1.2). In the last column the lattice constant has been calculated for each given peak using Eq. (3.1.1). Averaging these numbers gives a measurement of the lattice constant  $a = 4.79 \pm 0.01$  Å.

	20	$d = \lambda/(2\sin\theta)$	$d_A^2/d^2$	$3d_{A}^{2}/d^{2}$	Ν	hkl	а
А	32.28°	0.277 nm	1.00	3.00	3	111	0.480 nm
В	37.47°	0.240 nm	1.34	4.01	4	200	0.480 nm
С	54.11°	0.169 nm	2.68	8.03	8	220	0.479 nm
D	64.51°	0.144 nm	3.69	11.06	11	311	0.479 nm
Е	67.77°	0.138 nm	4.02	12.07	12	222	0.479 nm
F	80.18°	0.120 nm	5.37	16.10	16	400	0.478 nm
G	89.17°	0.110 nm	6.38	19.13	19	331	0.478 nm
Н	92.15°	0.107 nm	6.71	20.14	20	420	0.478 nm

 Table 3.1.
 The measured and calculated structural parameter of BAs crystal

I have also calculated our crystal density by

$$\rho = \frac{M \times n}{N_a \times a^3},\tag{3.1.3}$$

where  $\rho$  is density, M = 85.7326 (g/mol) is molar mass of BAs, n is the number of atoms in the unit cell which is 4 for FCC crystal structure,  $N_a = 6.022 \times 10^{23}$  is Avogadro's number, and  $a = 4.79 \times 10^{-8}$  cm is lattice constant. By plugging all these values in Eq. (3.1.3), we found  $\rho = 5.182$  (g cm<sup>-3</sup>).

# 3.2 Heat capacity measurement

A differential scanning calorimeter (DSC 404 C) was used to measure heat capacity (C<sub>P</sub>) of BAs crystal. Here, the system was programmed to increase the temperature of the BAs sample at 20 K min<sup>-1</sup>.



Figure 3.3. 77 mg BAs bulk sample was used to measure the heat capacity (C<sub>P</sub>)

We used a 77 mg BAs single crystal (Figure 3.3) grown by CVT in a sealed quartz tube as our sample for the C<sub>P</sub> measurement. Details of the growth procedure were explained in Sec 2.2. The X-Ray diffraction shown in Figure 3.4 confirms the single crystal nature of our grown crystals. The C<sub>P</sub> of the BAs single crystal was measured from 323 to 1123 K. The maximum temperature was set at 1123 K since BAs is expected to decompose at 1193 K (Lv *et al.*, 2015). Sapphire was used as the reference for this experiment since it has a well-defined C<sub>P</sub> over this temperature range.



Figure 3.4. Room temperature X-ray diffraction (XRD, Rigaku model SmartLab, Cu K-α1) confirming the single crystal nature of BAs crystals

The measured  $C_P$  and its fitted curve are shown in Figure 3.5. Additionally, the theoretical  $C_P$  of BAs at higher temperatures, which was calculated based on the classical limit predicted by the Dulong-Petit law for the Debye temperature of 700 K, is shown for comparison (Benkabou, Aourag, Becker, & Certier, 1999; Demidenko, Koshchenko,

Medvedeva, & Radchenko, 1975; Li *et al.*, 2018; Lucas Lindsay *et al.*, 2013). The C<sub>P</sub> gradually increases with increasing temperature and converges with the constant number 3NK from the Dulong-Petit law at high temperatures.



Figure 3.5. C<sub>P</sub> measured data and its fitted curve compared with calculated data. The uncertainty of the C<sub>P</sub> measurement is 5%

Generally, our measurement deviates from the calculated  $C_P$  by around 4% on average, which is within the 5% experimental error for the  $C_P$  measurement by DSC machine. However, there was a sharp peak of unknown origin at 1087 K. Based on our current knowledge, such a peak should not exist at this temperature for pure BAs. Therefore, to ensure it is not due to malfunctioning equipment, C<sub>P</sub> was measured three times on the same sample and the peak was observed for all measurements, as shown in Figure 3.5. Moreover, the peak was also present in the measurements of other crystals from different batches at exactly the same temperature. The change of enthalpy of the peak in Figure 3.5 is  $\Delta_r H$  (*peak*)  $\approx 0.9$  J g<sup>-1</sup>, but it generally varies in the range of 0.9 to 2.2 J g<sup>-1</sup> for different samples. This peak might be due to an impurity phase, for which we are carrying out further studies.

Next, the measured C<sub>P</sub> with respect to temperature was fit to a polynomial equation (Robie & Hemingway, 1995) as

$$C_p = aT^2 + bT + cT^{-0.5} + d, (3.2.1)$$

The resulting coefficients are  $a = 2.65 \times 10^{-5} \text{ J mol}^{-1} \text{ K}^{-3}$ ,  $b = -7.24 \times 10^{-2} \text{ J mol}^{-1} \text{ K}^{-2}$ ,  $c = -1.59 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-0.5}$ , and  $d = 1.43 \times 10^2 \text{ J mol}^{-1} \text{ K}^{-1}$ . Additionally, the RMSE<sup>1</sup> of the fitted curve is 0.7077 and the R-square<sup>2</sup> value is 0.9536, both of which indicate a good fit.

<sup>&</sup>lt;sup>1</sup> Root mean square error (RMSE) is a measurement of the differences between values observed and values predicted by model. RMSE is always non-negative and a value of 0 indicates a perfect fit to the data. <sup>2</sup> R-square is also an error measurement of the model. It is always in the range between 0 and 1 and a value

<sup>&</sup>lt;sup>2</sup> R-square is also an error measurement of the model. It is always in the range between 0 and 1 and a value of 1 indicates a perfect fit to the data.

# Chapter 4 Thermodynamic and theory of BAs SCs growth by chemical vapor transport

# 4.1 Introduction

Chemical vapor transport (CVT) has been the only method reported to grow BAs single-crystals (SCs) thus far. Although there has been significant development in growing BAs crystals using this method, challenges remain for the field, including improving the quality and size of the crystals and commercializing the BAs SC growth process (Tian & Ren, 2018). Studying the thermodynamic principles and theory underlying BAs SC growth using the CVT method are primary steps needed to address these challenges. To describe the transport reaction of this method quantitatively, we first need to quantify the thermodynamic properties of BAs so that the model calculations of the transport reaction can be carried out. Then, by using the calculated thermodynamic data of BAs, we study the theoretical concepts underlying the different approaches to BAs SC growth by the CVT method and compare the theoretical results with the experimental findings.

#### 4.2 Thermodynamic properties calculation

Previously, the thermodynamic properties of BAs have not been experimentally measured (Chu & Hyslop, 1972; H. Dumont & Y. Monteil, 2006) and thermodynamic data at high temperatures only have been available based on prediction and on the trend of variation of these properties in comparison with similar components (H. Dumont & Y. Monteil, 2006; H Dumont & Y Monteil, 2006). Here, we report the calculation of the

enthalpy (*H*), entropy (*S*), and Gibbs free energy (*G*), as well as the comparison of our results with the predicted data based on the measured heat capacity (C<sub>P</sub>) of BAs at high temperatures. Taking into account the discussion by Dumont and Monteil, (Alikhanyan, Steblevskii, Radchenko, & Gorgoraki, 1975; H. Dumont & Y. Monteil, 2006; H Dumont & Y Monteil, 2006) we accept that the enthalpy of formation and the entropy of BAs at room temperature are H<sub>f</sub> (298 K) = -30 kJ mol<sup>-1</sup> and S<sub>f</sub> (298 K) = 40 J mol<sup>-1</sup> K<sup>-1</sup>, respectively.

Table 4.1 shows the calculated enthalpy H (T), entropy S (T), and Gibbs free energy G (T) of BAs over the range of 298 to 1200 K, based on the equations

$$H(T) = H_f(298) + \int_{298}^{T} C_P \, dT,$$
  
$$S(T) = S_f(298) + \int_{298}^{T} \frac{C_P}{T} \, dT,$$
  
and  $G(T) = H(T) - T S(T).$ 

As a comparison for our results, Dumont and Monteil (H. Dumont & Y. Monteil,  
2006) predicted that H (800 K) 
$$\approx$$
 -15 kJ mol<sup>-1</sup>, S (800 K)  $\approx$  82 J mol<sup>-1</sup> K<sup>-1</sup>, and G (800 K)  
 $\approx$  -60 kJ mol<sup>-1</sup>, and we calculated that H (800 K) = -8.6 kJ mol<sup>-1</sup>, S (800 K) = 81.0 J  
mol<sup>-1</sup> K<sup>-1</sup>, and G (800 K) = -73.4 kJ mol<sup>-1</sup>. The measured entropy is in good agreement  
with the prediction, but there is a difference for the Gibbs energy and a significant disparity  
for the enthalpy.

Temp	Cp <sup>3</sup>	<b>S</b> (T)	[G (T) – H (298)]/T	G (T)	$H(T) - H_{f}(298)$	H (T)
K	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>
298.15	32.382	40.00	-40.00	-41.93	0.00	-30.00
300	32.561	40.20	-40.00	-42.00	0.06	-29.94
350	36.592	45.54	-40.41	-44.14	1.79	-28.21
400	39.439	50.62	-41.37	-46.55	3.70	-26.30
450	41.479	55.39	-42.67	-49.20	5.73	-24.27
500	42.954	59.84	-44.17	-52.08	7.84	-22.16
550	44.026	63.99	-45.78	-55.18	10.01	-19.99
600	44.809	67.86	-47.46	-58.48	12.24	-17.76
650	45.387	71.47	-49.17	-61.96	14.49	-15.51
700	45.819	74.85	-50.89	-65.62	16.77	-13.23
750	46.155	78.02	-52.59	-69.44	19.07	-10.93
800	46.429	81.01	-54.28	-73.42	21.39	-8.61
850	46.671	83.83	-55.93	-77.54	23.71	-6.29
900	46.905	86.51	-57.56	-81.80	26.05	-3.95
950	47.149	89.05	-59.15	-86.19	28.40	-1.60
1000	47.418	91.47	-60.70	-90.70	30.77	0.77
1050	47.726	93.79	-62.22	-95.34	33.15	3.15
1100	48.083	96.02	-63.71	-100.08	35.54	5.54
1150	48.498	98.17	-65.16	-104.94	37.96	7.96
1200	48.980	100.24	-66.58	-109.90	40.39	10.39

Table 4.1.Heat capacity, enthalpy, entropy, and Gibbs free energy of BAs over<br/>the temperature range of 298 – 1200 K

<sup>&</sup>lt;sup>3</sup> These are values predicted by the fitted curve.



# Figure 4.1. Enthalpy, entropy, and Gibbs free energy of BAs with respect to temperature

Dumont and Monteil (H. Dumont & Y. Monteil, 2006) also predicted a near-zero value for the BAs enthalpy at 1000 K. Figure 4.1 shows the calculated enthalpy, entropy, and Gibbs free energy of BAs with respect to temperature. Enthalpy rises monotonically with increasing temperature and reaches zero at 984 K, so the BAs formation reaction becomes endothermic at this temperature.

#### 4.3 Theory of BAs single crystals growth

To the best of our knowledge, chemical vapor transport (CVT) has been the only method reported to successfully grow BAs SCs to date. We studied three different CVT approaches for BAs SC growth by choosing different combinations of precursor sources. In this section, we describe each approach and analyze the underlying theory of each separately.

#### **4.3.1** BAs powder as precursor (First approach)

In earlier studies of BAs SC growth, BAs powder was initially prepared in a tube from a solid-state reaction of pure arsenic (As) and boron (B) at 1073 K (Ku, 1966; Lv et al., 2015). The stoichiometric BAs powder was then used as the precursor in another tube with a halogen as the transport agent to produce BAs SCs using the CVT method (Figure 4.2).



Figure 4.2 Schematic of approach one, BAs polycrystal as precursor without excess As
In this approach, the transport equation is defined as

$$BAs(s) + \frac{3}{2}X_2(g) \leftrightarrows BX_3(g) + \frac{1}{4}As_4(g) \qquad (X = I, Br, or CI),$$

We have analyzed the transport equation with three common halogens, iodine, bromine, and chlorine. To compare these reactions, the enthalpy of the reaction  $(\Delta_r H)$  at room temperature and the equilibrium constant (K<sub>P</sub>) at 900 K were calculated using equation  $\ln K_P = -\frac{\Delta_r G}{RT}$  for equilibriums

$$BAs(s) + \frac{3}{2}I_2(g) \leftrightarrows BI_3(g) + \frac{1}{4}As_4(g)$$

$$\Delta_r H(298 K) = 46.1 \, kJ \, mol^{-1} \qquad K_P \, (900 \, K) = 2.2 \, \times \, 10^{-3},$$
(4.3.1)

$$BAs(s) + \frac{3}{2}Br_2(g) \leftrightarrows BBr_3(g) + \frac{1}{4}As_4(g)$$

$$\Delta_r H(298 K) = -182.2 \ kJ \ mol^{-1} \qquad K_P (900 \ K) = 2.7 \times 10^{10},$$
(4.3.2)

and 
$$BAs(s) + \frac{3}{2}Cl_2(g) \leftrightarrows BCl_3(g) + \frac{1}{4}As_4(g)$$
 (4.3.3)  
 $\Delta_r H(298 K) = -334.6 \, kJ \, mol^{-1}$   $K_P(900 K) = 1.6 \times 10^{19}.$ 

The enthalpy values of reactions (4.3.2) and (4.3.3) are negative, and thus the reaction of BAs using chlorine or bromine is exothermic and any possible transfer would be from the cold end to the hot end. Additionally, as shown in Figure 4.3 since the equilibrium constant values of these two reactions are extremely high (KP  $>> 10^4$ ), CVT is not possible and these halogens are not suitable agents for BAs SC growth by CVT. No successful CVT experiments using either of these two halogens have yet been reported.



Figure 4.3. Equilibrium constant values of Eq. (4.3.1) to (4.3.3) over the temperature range of 900 to 1200 K

On the other hand, the reaction of BAs with iodine, reaction (4.3.1), is endothermic and the transfer direction is from the hot end to the cold end. It also has an equilibrium constant that lies within the acceptable range ( $10^{-4} < KP < 10^4$ ). Thus, iodine is the only suitable agent among those studied for obtaining BAs SCs using the CVT method (Chu & Hyslop, 1972). We therefore examined reaction (4.3.1) in more detail by plotting the partial pressure of the gaseous species. Figure 4.4 shows the partial pressure of all transport gaseous species in reaction (4.3.1). As can be seen in Figure 4.4, at lower temperatures, the partial-pressure values of the transport-effective species BI<sub>3</sub> and As<sub>4</sub> are very low, and the total pressure is mostly dominated by iodine, but as the temperature increases, the partialpressure values of BI<sub>3</sub> and As<sub>4</sub> slowly increase and the partial pressure of iodine drops slightly. Our analysis was limited to temperatures only up to 1200 K since the irreversible decomposition of BAs into B<sub>12</sub>As<sub>2</sub> is expected at higher temperatures.

To estimate the transport rate, we assume that CVT is performed on BAs powder with iodine in a tube that has a 10.5 mm inner diameter and is 25 cm long, with a coldzone temperature of 900 K and a hot-zone temperature of 1150 K (Lv *et al.*, 2015). According to Schäfer, (Schäfer) the transport rate of BAs can be calculated based on a diffusion approach with the equation (Binnewies et al., 2012) as



$$\dot{\mathbf{n}}(A) = \frac{\Delta P(C)}{\Sigma P} \frac{T^{0.75} \cdot q}{s} z,$$

Figure 4.4. Normalized partial-pressure values of the gaseous species P(i) which are normalized by the total pressure ( $\Sigma P$ ) of BI<sub>3</sub>, As<sub>4</sub>, and I<sub>2</sub> in the gas phase with respect to inverse temperature where  $\dot{n}(A)$  is the transport rate of substance A (mol h<sup>-1</sup>),  $\Delta P(C)$  is the partial pressure difference of transport-effective species C (bar),  $\Sigma P$  is the total pressure (bar), *T* is the mean temperature along the diffusion path (K), q is the cross section of the diffusion path (cm<sup>2</sup>), s is the length of the diffusion path (cm), and z is a coefficient used in this process, equal to  $0.6 \times 10^{-4} \mod K^{-1} \operatorname{cm}^{-1} h^{-1}$ . Using this equation,  $\dot{n}(BAs)$  is  $4.4 \times 10^{-6} \mod h^{-1}$  or  $0.37 \mod h^{-1}$ . Due to the low-pressure difference  $\Delta P(BI_3)$  over this temperature range, the transport rate is slow. Experimental findings also confirmed the slow rate of this approach, with SCs obtained in 2-3 weeks. (Lv *et al.*, 2015)

*Optimization:* We can significantly increase the transport rate by changing the tube dimensions and temperatures. Reducing the transport distance (tube length) and increasing the average temperature are easily achievable methods to optimize this approach without facing safety issues.

### 4.3.2 B powder with excess As as precursor (Second approach)

In another approach to BAs SC growth by CVT that is more commonly employed currently, B and As are used as precursors and are placed directly in the tube, rather than preparing BAs precursor separately (as described in section 4.3.1), along with iodine as the agent and extra As (Figure 4.5).



# Figure 4.5. Schematic of approach two using boron powder as precursor with excess As

In this case, since a more complex gas phase is formed, the chemical transport of BAs cannot be explained by just one reaction; several equilibrium reactions are important. This is a type of congruent transport and the number of equilibrium reactions (r<sub>u</sub>) is derived by the equation below (Binnewies *et al.*, 2012):

 $r_u = s - k + 1,$ 

where s is the number of possible gas species and k is the number of elements. The gas species (BI<sub>3</sub>, AsI<sub>3</sub>,  $As_4^*$ , As<sub>4</sub>, As<sub>2</sub>, I<sub>2</sub>, I) might occur in the sealed tube, so this leads to  $r_u = 5$ .  $As_4^*$  indicates arsenic that originates exclusively from the dissolution of BAs, as in reactions (4.3.5) and (4.3.6).

The equation

$$B(s) + \frac{1}{4}As_4(g) \to BAs(s)$$

$$\Delta_r H(298 K) = -68.3 kJ mol^{-1} \qquad K_P (900 K) = 35.7,$$
(4.3.4)

is one of the preliminary reactions that occurs in the tube, but since its product is solidstate, it cannot work as a transport equation. However, the BAs polycrystal produced by this reaction is used by reactions (4.3.5) and (4.3.6) for transportation to the other side of the tube and to create BAs SCs. Five equilibrium reactions that were used to determine the partial pressure of all possible gaseous species mentioned above, along with their reaction enthalpy values at room temperature and their equilibrium constant values at 900 K are (Bouix & Hillel, 1976, 1977)

$$BAs(s) + AsI_3(g) \leftrightarrows BI_3(g) + \frac{1}{2}As_4^*(g)$$
 (4.3.5)

$$\Delta_r H(298 K) = 113.6 kJ mol^{-1}$$
  $K_P(900 K) = 2.7 \times 10^{-6},$ 

$$BAs(s) + \frac{3}{2}I_2(g) \leftrightarrows BI_3(g) + \frac{1}{4}As_4^*(g)$$
 (4.3.6)

$$\Delta_r H(298 K) = 46.1 \, kJ \, mol^{-1}$$
  $K_P (900 K) = 2.2 \times 10^{-3},$ 

$$As_4(g) + 6I_2(g) \leftrightarrows 4AsI_3(g) \tag{4.3.7}$$

 $\Delta_r H(298 K) = -270 k mol^{-1}$   $K_P(900 K) = 4.0 \times 10^{11}$ 

$$As_4(g) \leftrightarrows 2As_2(g) \tag{4.3.8}$$

$$\Delta_r H(298 K) = 228.3 kJ mol^{-1}$$
  $K_P(900 K) = 4.3 \times 10^{-6},$ 

and 
$$I_2(g) \leftrightarrows 2I(g)$$
 (4.3.9)

 $\Delta_r H(298 K) = 151.3 \, kJ \, mol^{-1}$   $K_P(900 K) = 4.1 \times 10^{-4}.$ 

As shown in Figure 4.6, equilibriums (4.3.5) and (4.3.6) can contribute to the transport of BAs using the transport-effective species BI<sub>3</sub>, but the homogenous equilibrium

of the dissociation of arsenic and iodine plays no role in the mass transfer. Thus, we must calculate the solubility ( $\lambda$ ) of BAs in the gas phase to analyze the process of transportation.



#### Figure 4.6. Schematic of reaction chains in second approach

The solubility of the solid BAs in the gas-phase iodine and excess arsenic can be calculated as (Binnewies *et al.*, 2012; Binnewies, Glaum, Schmidt, & Schmidt, 2013):

$$\lambda(BAs) = \frac{n(B) + n(As^*)}{n(I) + n(As)} = \frac{P(BI_3) + P(AsI_3) + 4P(As_4^*)}{3P(AsI_3) + 3P(BI_3) + 2P(I_2) + P(I) + 4P(As_4) + 2P(As_2) + P(AsI_3)},$$
(4.3.10)

where n represents the balance of the molar numbers and P represents the partial pressure of the corresponding components. Figure 4.7 shows the solubility of BAs in the gas phase with respect to temperature. In systems with many equilibrium reactions, chemical transport usually takes place from the equilibrium region of higher solubility to the lower one (Binnewies, Schmidt, & Schmidt, 2017). Since the BAs solubility increases with temperature, the transportation is endothermic and should occur from the hot zone to the cold zone, which matches our experimental results (Binnewies *et al.*, 2012; Tian, Song, Chen, *et al.*, 2018).



# Figure 4.7. Solubility of BAs in gaseous iodine and arsenic with respect to temperature

To compare this approach with the previous one (section 4.3.1), we calculated its transport rate for the same tube dimensions and temperature range as for the previous calculation. The transport rate of this approach is proportional to the solubility difference between the source and sink temperatures,  $\Delta \lambda = \lambda(\text{source}) - \lambda(\text{sink})$ , and we need to replace the  $\frac{\Delta P(C)}{\Sigma P}$  term with  $\Delta \lambda$  in the Schäfer equation. For the same temperature range (1150 K  $\rightarrow$  900 K) and tube dimensions as in section 4.3.1, the transport rate is 0.59 mg h<sup>-1</sup>, which is almost 60% faster than that of the first method. Our experimental results also confirmed that this approach to BAs SC growth by CVT is faster than the first approach, with SCs obtained in less than 2 weeks (Tian, Song, Chen, *et al.*, 2018).

In Figure 4.8, by fixing the hot-zone temperature at 1150 K, we show the change of transport rate with respect to the cold-zone temperature for the same tube dimensions mentioned above for the second approach. Figure 4.8 shows that although the average temperature is reduced by reducing the cold-end temperature, the transport rate increases since  $\Delta\lambda$  increases. However, we should consider that the real temperature gradient depends on the capability of the tube furnace as well.



# Figure 4.8. Transport rate of BAs and average temperature with respect to the cold-zone temperature by fixing the hot-zone temperature at 1150 K

*Optimization:* By increasing the amount of excess arsenic, the rate of solubility of BAs in the gas phase can be increased, consequently increasing the transport rate. However, since excess arsenic increases the internal pressure of the tube and there is a strict limit to

the maximum working pressure of the quartz tubes, care must be taken when changing any of these parameters in order to avoid a tube explosion, which would cause toxic arsenic vapor to contaminate the environment.

### 4.3.3 BAs small crystal with excess As as precursor (Third approach)

In the third investigated approach, small BAs SCs obtained using one of the previously described approaches are used as the precursor and are placed in a sealed tube along with excess arsenic and iodine as the agent Figure 4.9.



# Figure 4.9 Schematic of third approach, BAs small crystals as precursor with excess As

This approach uses small BAs SCs as a pure source to obtain BAs SCs of larger size and higher quality, as Xing discussed in (Xing, Chen, et al., 2018), although we used a different transport agent (I<sub>2</sub>) than that used in the previous study (TeI<sub>4</sub>). As shown in Figure 4.10, all of the reactions discussed for the second approach (section 4.3.2) are applicable to this approach except reaction (4.3.4).

Bi <sub>a</sub> (s	
BAs (s) + 3/2 $I_2(g) \Rightarrow BI_3(g) + \frac{1}{4}As_4(g)$	$BI_{3}(g) + \frac{1}{4}As_{4}(g) \Rightarrow \frac{3}{2}I_{2}(g) + BAs (s)$
$BAs(s) + Asl_3(g) \Rightarrow Bl_3(g) + V_s As_4(g)$	$Bl_3(g) + \frac{1}{2}As_4(g) \Rightarrow Asl_3(g) + BAs(s)$
ا, (g). Asi	(g) BAS SCS

Hot zone

Cold zone

#### Figure 4.10. Schematic of reaction chains in third approach

Since reaction (4.3.4) is not considered a transport equation and was not directly involved in our calculation, our analysis here is the same as for the second approach, except that in this case, BAs is ready to transfer from the beginning of the process, so faster transport is observed in this approach. As explained in section 4.3.2, the product of reaction (4.3.4), BAs, is used by equations (4.3.5) and (4.3.6) for transportation, and since this reaction is slow, we expect that replacing B powders with previously obtained BAs SCs would make the transportation faster. Experiments in Ref. (Xing, Chen, *et al.*, 2018) confirm this expectation; additionally, more and thicker crystals form at the cold end when using the BAs precursor, which shows that the transport rate of this approach is faster than that of the other two.

*Optimization*: As in the second approach (section 4.3.2), the transport rate of this approach can be increased by using additional excess arsenic, and the optimizations mentioned in section 4.3.1 can be applied to this approach as well.

### 4.4 Discussion and comparison

Three approaches to BAs SC growth by CVT using different combinations of precursors have been analyzed, and each has advantages and disadvantages, which are discussed below. The first approach (section 4.3.1) has a slow transport rate, resulting in slow SC growth, but not requiring excess arsenic in the tube is a potential advantage. Excess arsenic builds up internal pressure, so the lack of excess arsenic makes the first approach more flexible for changing the tube dimensions to optimize this approach without being concerned about reaching the maximum working pressure and causing the tube to explode. With the flexibility provided by this approach, our analysis shows that choosing tubes with shorter lengths would efficiently increase the transport rate.

The best quality BAs SC obtained thus far has been made by using the second approach (section 4.3.2) (Kang *et al.*, 2018; Li *et al.*, 2018; Tian, Song, Chen, *et al.*, 2018). Crystals made employing this approach have shown near-calculated thermal conductivity values, which is an indication of having fewer defects. However, research has shown that boron powder, which is not 100% pure, is a source of impurities in the crystals (Chae et al., 2018; Lyons et al., 2018). Thus, using boron powder directly in tube is a weakness of the second approach and a source of contamination. The third approach (section 4.3.3) has the advantage of using pre-selected pure BAs SCs with relatively higher thermal conductivity as the source, which can be considered as a source-purifying step.

Additionally, in both the second and third approaches, excess arsenic has an important role in controlling the transport rate. We have shown that the third approach has a higher transport rate and results in more crystals at the cold end. Although the crystals include defects, imperfections, and holes, these issues can be explained by the lack of good nucleation techniques and of adequate space for crystal growth, which forces the crystals either to merge or to grow on top of one another. However, the third approach, with its faster transport rate and its use of a purer material as the growth source, has good potential to be superior to the other two approaches in terms of the size and quality of crystals obtained.

## Chapter 5 Thermal conductivity measurement using steady state method

### 5.1 Introduction

There are several methods to measure thermal conductivity of material. Time domain thermo reflectance (TDTR) is one of the famous methods which is notably used for thermal conductivity measurement of thin film materials (Cahill, 2004; Wilson & Cahill, 2014). This method measures the thermal conductivity without contact with sample directly, so it avoids the temperature measurement issues such as heat loss and measurement error. In this method, the thermal conductivity can be obtain at certain positions by changing the laser spot size ( $1 \sim 100 \ \mu m$ ) (Tian & Ren, 2018). This method has shown a maximum thermal conductivity of 1300 W m<sup>-1</sup> K<sup>-1</sup> at room temperature for BAs single crystal (Kang *et al.*, 2018). On the other hand, growing BAs SCs longer than 4 mm makes  $\kappa$  measurement using the steady state (SS) method possible. Thus, this method was employed to measure the thermal conductivity of BAs in our lab.

### 5.2 Steady state method

In this method, a silicon bar is used as reference and is attached to the heat source (resistive heater). The sample is attached to reference from one side and to the sink from other side as it was shown in the Figure 5.1. Ignoring the heat loss through thermocouples and the contact thermal resistance errors between thermocouples and sample surfaces, we

can use one dimensional Fourier heat transport equation to find the thermal conductivity of sample as (Tian, Song, Chen, *et al.*, 2018)



Figure 5.1. The schematic of steady state method for measurement of thermal conductivity

$$Q = A_r \kappa_r \frac{\Delta T_r}{\Delta X_r} = A_s \kappa_s \frac{\Delta T_s}{\Delta X_s}$$
 and (5.1)

$$\kappa_s = \frac{A_r}{A_s} \frac{\Delta T_r}{\Delta T_s} \frac{\Delta X_s}{\Delta X_r} \kappa_r, \qquad (5.2)$$

where  $\kappa$  is thermal conductivity, A is cross section area,  $\Delta T$  is temperature difference,  $\Delta X$  is the distance between two thermocouples, subscript r shows the label for reference, and subscript s for sample. For one-dimension assumption to be correct in Eq. (5.1), a long bar shape BAs sample with dimension of  $0.28 \times 0.49 \times 2 \text{ mm}^3$  was prepared using polishing. A long silicon bar with dimension of  $0.52 \times 0.57 \times 4 \text{ mm}^3$  was also used as reference which was cut and polished from a silicon wafer. The thermal conductivity of silicon wafer was measured with Physical Property Measurement System (PPMS) Quantum Design as shown in Figure 5.2. We cannot use PPMS to measure  $\kappa_{BAs}$  directly because a needle shape

sample with minimum geometry of  $10 \times (1 \times 1) mm^3$  is required per PPMS machine, Thermal Transport Option (TTO) user's manual.



## Figure 5.2. Thermal conductivity of silicon with respect to temperature measured by PPMS

A resistive heater was used as source and epoxy was applied to join all connections as shown in Figure 5.1. Four thermocouples (Omega CHAL - 002) with diameter 50  $\mu$ m were also attached on the sample and reference surface using superglue to measure temperatures T<sub>1</sub> through T<sub>4</sub> in Figure 5.1. Sample, reference, and resistive heater were suspended by being attached to a sink with constant temperature of 10 <sup>o</sup>C. The whole setup was enclosed by a copper shield and located in a chamber that was evacuated to 10<sup>-6</sup> torr by a turbo pump. Thus, heat loss through radiation and convection can be ignored and it is a good assumption that the whole heat flows through silicon, passes through BAs bar. Using Eq. (5.2), the measured  $\kappa_{BAs}$  with respect to heat source temperature (T<sub>1</sub>) was shown





Figure 5.3. The thermal conductivity of BAs measured by steady state method

As shown in Figure 5.3, using SS method the thermal conductivity of BAs was measured around 417 W m<sup>-1</sup> K<sup>-1</sup> which is much lower than the predicted value and the reported measurement values with TDTR method. The disadvantage of SS method is the restriction in choosing BAs samples. Since there are huge amount of stresses and tensions involve in sample preparation such as polishing, installation, and measurement, only thicker samples can be used in this method. On the other hand, experiments show that thicker BAs samples involve more voids and defects which reduce the thermal conductivity of crystals. That is, we basically have to pick BAs crystals as sample which we originally know they have low quality.

### 5.3 Uncertainty of measurement

We have also calculated the uncertainty of this measurement. As per manufacturer spec, the error of the thermocouples is  $1.1 \,^{0}$ C or 0.4% of reading whichever is greater which  $1.1 \,^{0}$ C is applicable in the range of our temperature reading. Only considering the thermocouple's uncertainties and using Eq. (5.2), we found the thermal conductivity measurement error as

$$\Delta T_1 = (T_1 \pm 1.1 \,^{\circ}C) - (T_2 \pm 1.1 \,^{\circ}C), \tag{5.3}$$

$$\Delta T_2 = (T_3 \pm 1.1 \,^{\circ}C) - (T_4 \pm 1.1 \,^{\circ}C), \tag{5.4}$$

$$\delta_{\Delta T_1} = \delta_{\Delta T_2} = \sqrt{\delta_{T_1}^2 + \delta_{T_2}^2} = \sqrt{1.1^2 + 1.1^2} = 1.6 \,^{\circ}C, \quad (5.5)$$

and 
$$\delta_{\kappa_s} = \frac{\Delta T_2 \pm \delta_{\Delta T_1}}{\Delta T_1 \pm \delta_{\Delta T_1}} = \left(\frac{\delta_{\Delta T_1}}{\Delta T_1} + \frac{\delta_{\Delta T_2}}{\Delta T_2}\right) = \left(\frac{1.6}{\Delta T_1} + \frac{1.6}{\Delta T_2}\right).$$
 (5.6)

Considering errors  $\delta_{\Delta x} = \pm 0.05$  mm,  $\delta_A = \pm 5$  %, and  $\delta_{Kr} = \pm 3.5$  %, the total uncertainty of  $\kappa_{BAs}$  measurement is calculated as

$$\delta_{\kappa_{s}} = \frac{A_{r}(\pm 5\%)}{A_{s}(\pm 5\%)} \frac{(T_{1}\pm 1.1\ ^{\circ}C) - (T_{2}\pm 1.1\ ^{\circ}C)}{(T_{3}\pm 1.1\ ^{\circ}C) - (T_{4}\pm 1.1\ ^{\circ}C)} \frac{\Delta x_{s}(\pm 0.05\ mm)}{\Delta x_{r}(\pm 0.05\ mm)} \kappa_{r}(\pm 3.5\%)$$
(5.7)

and 
$$\delta_{\kappa_s} = \delta_{A_r} + \delta_{A_r} + \left(\frac{\delta_{\Delta T_r}}{\Delta T_r} + \frac{\delta_{\Delta T_s}}{\Delta T_s}\right) + \left(\frac{\delta_{\Delta X_r}}{\Delta X_r} + \frac{\delta_{\Delta X_s}}{\Delta X_s}\right) + \delta_{\kappa_r}.$$
 (5.8)



# Figure 5.4 Uncertainty of BAs thermal conductivity measurement with steady state method

Figure 5.4 shows the total measurement error affected by considering all uncertainties is around 63% in average which shows  $\kappa_{BAs} = 417 \pm 175$  W m<sup>-1</sup> K<sup>-1</sup>. This uncertainty is very large. Figure 5.4 also shows that 42% of uncertainty is because of the thermocouples' and their heat losses.

### 5.4 Heat loss measurement

Therefore, I tried to measure the heat loss through thermo couples by employing SS method on one solid silicon bar with dimension  $0.52 \times 0.53 \times 9 \text{ mm}^3$  as shown in Figure 5.5. In this figure, the heat losses through thermocouples was considered, unlike Figure 5.1. In this calculation the control volume (CV) begins right after the first

thermocouple and ends right before the forth one, so we only consider the heat loss through the two middle thermocouples. Therefore, the total heat loss (q) is

$$\mathbf{q} = \mathbf{q}_2 + \mathbf{q}_3$$

Thus, Eq. (5.1) will be updated by including total heat loss as

$$Q = \kappa A \frac{T_1 - T_2}{\Delta X_1} = \kappa A \frac{T_3 - T_4}{\Delta X_2} + q.$$
 (5.9)

Solving Eq. (5.9) for q, we have

$$q = \kappa A \left[ \frac{\Delta T_1}{\Delta X_1} - \frac{\Delta T_2}{\Delta X_2} \right].$$
(5.10)



### Figure 5.5. Schematic of heat loss measurement with SS method using Silicon

Figure 5.6 shows the heat loss (q) with respect to  $T_1$  measured by applying Eq. (5.10). This heat loss is negative which physically doesn't make sense and it supposed to be due to measurement errors.



### Figure 5.6. Heat loss through thermocouples in SS measurement using silicon

To find the reason of this issue, we did more analysis on the measurement error by calculating the uncertainty of temperature gradients in Eq. (5.10) by considering thermocouples uncertainties but ignoring the  $\Delta X$  uncertainties as

$$\nabla T = \nabla T_1 - \nabla T_2 = \frac{\Delta T_1}{\Delta X_1} - \frac{\Delta T_2}{\Delta X_2}$$
 and (5.11)

$$\delta_{\nabla T} = \delta_{(\nabla T_1 - \nabla T_2)} = \sqrt{\left(\frac{\delta_{\Delta T_1}}{\Delta X_1}\right)^2 + \left(\frac{\delta_{\Delta T_2}}{\Delta X_2}\right)^2}.$$
(5.12)

Using information in Eq. (5.5) we have

$$\Delta X_1 = 2.91 mm,$$
$$\Delta X_1 = 2.1 mm,$$

and 
$$\delta_{\Delta T} = \delta_{(\Delta T_1 - \Delta T_2)} = \sqrt{\left(\frac{1.6}{2.9}\right)^2 + \left(\frac{1.6}{2.1}\right)^2} = \pm 0.94.$$
 (5.13)

Figure 5.7 confirms that the measured  $\nabla T$  Eq. (5.11) is within the measurement uncertainty of  $\pm$  0.94 and it is not reliable, so the negative heat loss is due to thermocouple measurement errors and is not accurate.



Figure 5.7. The temperature gradient in heat loss measurement using silicon

Therefore, to measure the thermocouple's heat loss, we repeated this experiment on a material such Sapphire (Al<sub>2</sub>O<sub>3</sub>) with lower thermal conductivity around 36 W m<sup>-1</sup> K<sup>-1</sup> at room temperature (Figure 5.8). We have plotted the heat loss through thermocouples with respect to source temperature (T<sub>1</sub>) using sapphire in Figure 5.10. This figure shows that heat loss is positive and constantly increases in the whole range of temperatures.



Figure 5.8. Schematic of heat loss measurement with SS method using Sapphire



Figure 5.9. Thermal conductivity of Sapphire measured by PPMS



### Figure 5.10. Heat loss through thermocouples in SS measurement using Sapphire

Doing the same calculation, the uncertainty of temperature gradient Eq. (5.12) on sapphire is  $\delta_{\Delta T} = \pm 0.73$  and it has been plotted in Figure 5.11 which shows that our measurement is reliable since  $\nabla T$  is out of error threshold in temperatures above  $T_1 = 33^{\circ}$ C. To see how large the heat loss is, we have calculated the ratio of heat loss (q) over the total heat flow (Q) and plotted in Figure 5.12. This shows that heat loss is around 33% of the total heat flow which is a large amount and can cause a huge uncertainty in our measurement as we saw in  $\kappa_{BAs}$  measurement.



Figure 5.11. The temperature gradient in heat loss measurement using Sapphire



Figure 5.12. The ratio of heat loss over total heat flow

To confirm our finding regarding heat loss measurement, we have repeated this experience on two more materials, one is copper with high thermal conductivity around 408 W m<sup>-1</sup> K<sup>-1</sup> at RT (Figure 5.13) and the other one a thermoelectric material with chemical formula ( $ZrCoSb_{0.8}Sn_{0.2}$ ) with low thermal conductivity of around 6 W m<sup>-1</sup> K<sup>-1</sup> at RT (Figure 5.14) that we call it ZCSS for simplicity.



Figure 5.13. Thermal conductivity of Copper measured by PPMS



Figure 5.14. Thermal conductivity of ZCSS measured by PPMS

Heat loss of thermocouples have been calculated by employing Eq. (5.9) on both copper and ZCSS and the results have been plotted in Figure 5.15 and Figure 5.16 respectively. As we can see in Figure 5.15, the heat loss on copper is negative in some temperatures and so wavy but on ZCSS Figure 5.16 it is positive and constantly increases. Thus, we plotted the temperature gradient for both copper and ZCSS in Figure 5.17 and 5.18 respectively. Using Eq. (5.12), the temperature gradient threshold of uncertainty for copper is  $\delta_{\Delta T} = \pm 0.63$  and for ZCSS is  $\delta_{\Delta T} = \pm 1.05$ .



Figure 5.15 Heat loss through thermocouples in SS measurement using Copper



Figure 5.16 Heat loss through thermocouples in SS measurement using ZCSS



Figure 5.17 The temperature gradient in heat loss measurement using Copper



Figure 5.18 The temperature gradient in heat loss measurement using ZCSS

Since temperature gradient for ZCSS is out of the uncertainty threshold, it is reliable and accurate. However, this data for copper is within the error threshold so it is not reliable. Figure 5.19 compares the thermocouples heat loss on sapphire and ZCSS and it shows that the results are very close. The heat loss is around 3 mW at 20  $^{\circ}$ C and constantly increase with temperature and reach to around 13 mW at 60  $^{\circ}$ C.



Figure 5.19. Comparison of thermocouple heat loss in SS measurement over Sapphire and ZCSS

### 5.5. Results and Discussions

Using SS method, we measured the thermal conductivity of BAs around  $417 \pm 175$  W m<sup>-1</sup> K<sup>-1</sup> which was much smaller than TDTR method (over 1000 W m<sup>-1</sup> K<sup>-1</sup>) and has a large uncertainty. We explained this gap with the type of crystal that we had to choose in

SS method so that it can tolerate the huge stress involve in sample preparation in this method. Thus, one way to improve this method can be using dicing saw machine to cut our samples instead of polishing. We can choose thinner and consequently higher quality crystal with dicing saw machine since less stress is applied to crystal during sample preparation compare to polishing. Dicing machine is also more accurate in cutting sample and reference bars so it reduces the uncertainty of cross section area ( $\delta_A$ ) and total uncertainty of thermal conductivity measurement ( $\delta_{\kappa}$ ).

As we analyzed above, big portion of our total uncertainty is because of thermocouples and their huge percentage of heat loss. We can improve our measurement by using thinner thermocouples. The current thermocouples which we used in these experiments had the diameter of 50  $\mu$ m but as of my knowledge thinner thermocouples with diameter 12.5  $\mu$ m are also available that means its diameter is 4 times smaller, so its heat loss is almost 16 times less than the current one which it causes much smaller uncertainty in measurement. This change can significantly improve our total uncertainty which is already 63%.

### **Chapter 6** Conclusions and future works

We have growth BAs single crystal over 4 mm length using chemical vapor transport (CVT) method. Time-domain thermo reflectance (TDTR) method shows the ultrahigh thermal conductivity value up to 1300 W m<sup>-1</sup> K<sup>-1</sup> in our grown crystals which is the highest among semiconductor materials. But, using steady state method we just measured the thermal conductivity of 417 W m<sup>-1</sup> K<sup>-1</sup> due to thick crystal with more defects we had to choose for sample preparation. However, even this reported thermal conductivity value of BAs is higher than that of many common high thermal conductivity materials like copper, gold, aluminum, etc. Therefore, the high thermal conductivity of BAs, along with its better mechanical performance than the most used material, silicon, make it a good candidate for future electronic devices.

The X-Ray diffraction shows that our BAs single crystals has FCC crystal structure with the lattice constant of  $4.79 \pm 0.01$  Å. We also calculated the density of BAs to be 5.182 g cm<sup>-3</sup>. We measured the heat capacity of a BAs sample with respect to temperature and compared our experimental results to the previous theoretical data.

We calculated the enthalpy, entropy, and Gibbs free energy for BAs in range of 298 to 1200 K and compared our results with the previously predicted values. We found that the BAs formation reaction becomes endothermic at 984 K.

Finally, BAs SC growth using the chemical vapor transport method was further analyzed using thermodynamic concepts. Three approaches to growth using different combinations of precursors were explained theoretically and these analyses were compared with experimental results. By considering the advantages and disadvantages of each approach, we concluded that using a precursor combination of small BAs SCs with excess arsenic has the fastest transport rate and has good potential for growing better BAs SCs.

Future work 1:

Recent research on p-type conductivity of the BAs SC has shown that contaminant elements such as silicon and carbon are prime candidates for reducing the experimental value from the prediction. (Lyons et al., 2018) Therefore, eliminating these contaminants could be a good strategy for increasing thermal conductivity.

Future work 2:

As explained in Sec. (4.3.3), using BAs small crystal as precursor (Third approach) increases the rate of transportation so we will have bigger and greater number of crystals on growth side, but most of them are thick with dark color which are signs of defects and low-quality crystals. We need to improve our nucleation skills to control the crystal growth better in higher transport rate.

## **Publications**

**Ziyaee, Hamidreza**, Geethal Amila Gamage, Haoran Sun, Fei Tian and Zhifeng Ren. "Thermodynamic Calculation and Its Experimental Correlation with the Growth Process of Boron Arsenide Single Crystals." *Journal of Applied Physics* 126, no. 15 (2019): 155108.

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