

Achieving Ultrahigh Thermal Conductivity and Carrier Mobility in Boron Arsenide Single
Crystals

by
Geethal Amila Gamage Udalamatta Gamage

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Chair of Committee: Zhifeng Ren

Committee Member: Paul C. W. Chu

Committee Member: Gemunu Gunaratne

Committee Member: Shuo Chen

Committee Member: Arnold Guloy

University of Houston
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ABSTRACT

Thermal management becomes a critical technological challenge in the modern microelectronics world, including high power density electronics such as microprocessors, high-power radio frequency (RF) devices and optoelectronic devices. When modern electronic devices are made at very small sizes, excess heat generation rises, which reduces the device's performance, efficiency and life span. Materials with high thermal conductivity are crucial to improve the performance and reliability of such devices. In theory, heat is transferred via conduction, convection and radiation, of which direct conduction is the easiest and fastest way. Thus, researchers are looking for materials with higher thermal conductivity, but developing a passive cooling solution that is both cost-effective and reliable has been very challenging because of the difficulties in synthesis, high cost and the requirement of extreme laboratory conditions.

Boron arsenide (BAs) with zinc blende structure has been predicted to have an ultrahigh thermal conductivity close to $2000 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature by first-principle calculations, which close to diamond. However, experimental synthesis for large-scale proved to be extremely challenging, due to spontaneous nucleation and slow growth rates. Here we report an enhanced CVT growth of BAs single crystals with more controlled nucleation and optimized growth parameters for the purpose of achieving very high thermal conductivity. We have obtained high-quality BAs single crystals with the largest size of 7 mm and highest thermal conductivity of $1240 \text{ W m}^{-1} \text{ K}^{-1}$ grown using GaAs wafers, which is much higher than most of the industry-leading heat sink materials.

Furthermore, we performed electrical and optical characterizations on high-quality BAs and obtained bulk carrier mobility of $650 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by transport method and local

mobility of $\sim 1500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by optical method. From optical measurements, we obtained an indirect bandgap of 2.0 eV for BAs, which proven that BAs is the only known wide bandgap semiconductor to have ultrahigh thermal conductivity. Such enhancements make BAs suits for more and more characterizations and leading to new research of potential future semiconductor applications. Further improvements on BAs seem to be very promising towards extensive fundamental studies and industry applications.

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CHAPTER 1 INTRODUCTION

1.1 Background

With the miniaturization of microelectronic devices, heat management has become one of the largest challenges in the modern electronic industry. With fast-growing industry standards and shrinking sizes, materials with high thermal conductivities are important to cool devices such as high-power-density electronics and optoelectronics. Compared to heat transport by convection and radiation, heat is mostly transferred via conduction in many metallic and semiconductor materials. However, the industry-leading thermal conductor materials still have limitations, which rigorously restrict the working temperatures of many electronic devices. Thermal insulators like diamond and carbon nanotubes are too expensive and challenging to produce due to extreme synthesis procedures.

Recently, differing from common criteria, researchers reported zinc-blende boron arsenide (BAs) has an ultra-high thermal conductivity of over $2000 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature by first-principles calculations, which is comparable to diamond, which holds the highest thermal conductivity in bulk materials.¹ However, the growth of BAs single crystals with high thermal conductivity close to predicted values and larger in size is very difficult to achieve due to many challenges. BAs crystals have been previously grown by the chemical vapor transport (CVT) method, but the non-uniformity and defects are mainly incorporated with the resulted crystals.^{2, 3} Such major issues slow down the research on BAs for further experimental trials and use in device applications. We reported the growth of millimeter - scale BAs bulk crystals with local room-temperature thermal conductivity exceeding $1000 \text{ W m}^{-1} \text{ K}^{-1}$ and average bulk value exceeding $900 \text{ W m}^{-1} \text{ K}^{-1}$ respectively.⁴ At the same time BAs single crystals have been confirmed to have a moderate indirect bandgap of $1.9 - 2.0 \text{ eV}$ at

room temperature, and thus, BAs is the only high thermal conductor material with wide bandgap semiconductor nature.⁵⁻⁸

1.2 Fundamentals of Thermal Conductivity

Thermal conductivity (κ), refers to the ability of a material to transfer heat by conduction. In general, thermal conductivity is defined by Fourier's Law for heat conduction which discussed later in this chapter. It depends on the property of material to flow the heat, which is mainly carried by electrons and phonons. For instance, metals have high thermal conductivity with high efficiency of conducting heat, while the insulators have low thermal conductivity.

1.2.1 Electrical Thermal Conductivity

In metals, heat is mainly carried by valence electrons. Since electrons also carried the electric charge the electrical conductivity is proportional to thermal conductivity (κ_e). This behavior is first reported by Gustav Wiedemann and Rudolph Franz in 1853, which named as Wiedemann-Franz law.⁹ It expressed as;

$$\kappa_e = L\sigma T$$

Where L is the proportionality constant, known as the Lorenz number, κ_e is the thermal conductivity driven by electrons, σ is the electrical conductivity, and T is the temperature. However, when temperature rises the vibrations of electrons increase, thus increases resistance and hence decrease its electrical conductivity. Widely used commercial thermal conductor like copper and aluminum also have κ_e limitations at higher temperatures due to low electrical conductivity. Due to such limitations in electrical conductivity,

researches cannot improve the material properties of any metal to obtain high thermal conductivity.

1.2.2 Lattice Thermal Conductivity

In addition to electrons, heat can also transport via the atomic vibrations given by the phonons in lattice structure. This primarily happens in semiconductors and insulators, which can be derived as lattice thermal conductivity (κ_L) given by,

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

where V is the crystal volume, $C_{\lambda} = k_B n_{\lambda}^0 (n_{\lambda}^0 + 1) \times (\hbar\omega_{\lambda}/k_B T)^2$ is the specific heat per phonon mode, k_B is the Boltzmann constant, and $n_{\lambda}^0 = 1/[\exp(\hbar\omega_{\lambda}/k_B T) - 1]$ is the Bose factor, and ω_{λ} is the phonon frequency. The sum is over all phonon modes, $\lambda = (\mathbf{q}, j)$, with the wave factor $\mathbf{q}$ and the polarization j . We define $\kappa_{\alpha\alpha} = \kappa$, and also $v_{\lambda\alpha}$ and $\tau_{\lambda\alpha}$ are the velocity component and the phonon transport lifetime along a cubic direction α for the assumed small T gradients.^{1, 10} Since longitudinal waves have a much greater phase velocity than transverse waves, the relaxation length or mean free path of longitudinal phonons will be much greater. Thus, thermal conductivity will be largely determined by the speed of longitudinal phonons. Since the acoustic phonons have large energy dispersion and therefore scattering of acoustic phonons will majorly affect κ_L , only limited by lattice defects such as vacancies, grain boundaries, dislocations, etc.

1.3 Single Crystal Growth

Single crystal is a solid material has the same lattice structure, which has continuous three-dimensional arrangement of the atoms or molecules repeated throughout the volume.

Single crystals are one of the highly dominant materials in the electronics industry due to its continuous, uniform and highly ordered structure which entitle them to have some unique properties. Even with the advanced development of polycrystalline materials, single crystals showcase extensive use in optical, microelectronic and optoelectronic applications such as light-emitting diodes (LEDs), photodetectors, wide-bandgap devices, high-power electronics, etc. There are four general techniques for the growth of single crystals: growth from solid, melt, solution and vapor phase. Specific techniques to produce high-quality single crystals include the Czochraski process, Bridgman technique and the epitaxial thin film deposition. The growth of single crystals is a challenging task, which depends on the characteristics of the material, such as melting point, volatility and solubility in water or other solvents.

1.3.1 Grown from Solid

Solid-state crystal growth (SSCG) has become a critical technique in the development of high-quality single crystals with complex chemical compositions. SSCG is appeared as a promising alternative by its lower growth temperatures than conventional melt and solution growth techniques by producing crystals through a solid phase transformation of a polycrystalline matrix into a single crystal. This allows for higher chemical homogeneity and volatility control, while remaining as a cost-effective and simplistic processing in growth.¹¹ Since this is only low temperature technique, this method may not be a preferred alternative to grow single crystals with high thermal conductivity.

1.3.2 Grown from Solution

In solution growth, crystals are grown from aqueous solution like water, ethanol, acetone, etc.¹² This method is widely used in producing bulk crystals in four major categories.

- i. Low temperature solution growth
- ii. High temperature solution growth
- iii. Hydrothermal growth
- iv. Gel growth

In low temperature solution growth solvents like water, ethyl alcohol, acetone, etc. are used in with different techniques like slow cooling, solvent evaporation and temperature gradient. Single crystals like $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and KH_2PO_4 are grown in this method.¹³

Similarly, hydrothermal growth depends on the solubility of minerals in aqueous solutions under high temperature and high vapor pressure. The hydrothermal method has some advantages over the other techniques as far as the purity, crystal symmetry, reproducibility, low crystallization temperature, fast reaction times, lower energy requirements, etc. In this method crystal growth happens under hydrothermal conditions requires an apparatus capable of containing highly corrosive solvent at high temperature and pressure over a long period of time.¹⁴

In the growth of crystals from high temperature solutions, also known as flux growth, the constituents of the material to be crystalized are dissolved in a solvent and re-crystallization occurs when the solution becomes supersaturated.¹⁵ Many metallic structures like borates, LiNbO_3 , BaTiO_3 , BaB_2O_4 and others are grown this way. However, due to the lack of information and incompleteness of binary and trinary phase diagrams, the choice of proper solvent or flux becomes a major problem and limits the growth from flux. Furthermore, removing the crystals from the solvent is a challenging task, which can easily damage the crystals.

1.3.3 Grown from Melt

This method is the most widely used technique in single crystal growth and it is a process of crystallization of fusion and re-solidification of material where crystallization occurs from a melt on cooling liquid phase. Melt growth is commercially available for growth of industry leading semiconductors like Si. This can be further divided into subcategories with various techniques like Bridgmann process, Czochraski process, zone melting process, etc.

In this technique apart from container and surrounding atmosphere, no impurities are introduced in growth process and the growth rate is much higher to obtain large size single crystals. The Czochraski process is one of the most common for the production of single crystals for electronic and optical devices, such as Si and Ge single crystals.¹⁶ This method allows the growth of large single crystals in a relatively short time. The growth of single crystal process can be carried out in a horizontal or vertical geometry. In Czochraski process, growth direction is mainly vertical but in other crucible methods like Bridgman process for growth of lithium fluoride (LiF) and zone melting process for Si and Ge, can be either vertical or horizontal.^{17, 18} However, it also has some disadvantages like difficulty in keeping constant temperature during the crystal growth and achieving very high melting points for some materials, reaction of the melted material with the crucible and high production costs.¹¹

1.3.4 Grown from Vapor Phase

Crystallization from vapor is widely adopted to grow bulk crystal, epitaxial films, and thin coatings. Even though, growth from melt is widely used in manufacturing industry, wide range of single crystal growth process in vapor phase.¹⁹ The growth of single crystals from the vapor phase can be achieved via multiple steps like sublimation process, gas phase reaction,

and transport reaction. Techniques for growing crystals from vapor is divided into two main types;

- i. Chemical vapor transport
- ii. Physical vapor transport

Compared to the melt growth process, vapor phase growth requires low temperature condition thus result in a significantly higher quality crystals due to impurities from the sources, structural and compositional uniformities and phase transitions.

1.3.4.1 Chemical Vapor Transport

In the chemical vapor transport (CVT) method, materials are transported as a chemical compound mostly halide, in the gas phase, which decomposes in the growth region. In this case depending on the thermodynamic reactions, growth region can be either hotter or colder than the source side. It is a heterogeneous reaction which is started with solid or liquid source material in condensed phase, has an insufficient pressure for its own sublimation or distillation. But in a presence of a gaseous reactant, the transport agent, reactions taken place and deposits in another place. This deposition take place in a position where the external conditions satisfy the chemical equilibrium at that position of recrystallization. Usually, temperature gradient technique is applied for this sublimation and recrystallization process (Figure 1.1).²⁰

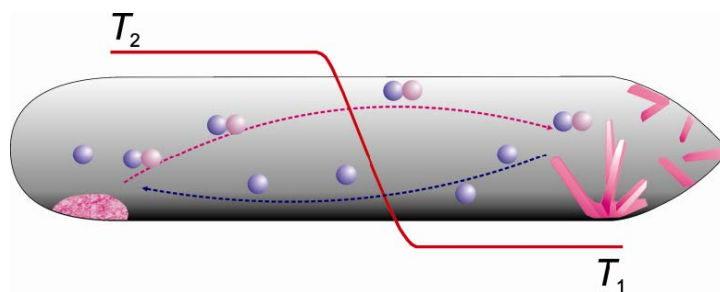


Figure 1.1 Schematic of CVT setup for crystallization of solid source in a temperature gradient.¹⁹

CVT helps to form pure and crystalline solids like single crystal materials, which has a high value because of the use in semiconductor industry. A systematic research of CVT was carried out by Schafer in the 1906s, and it became apparent that crystalline species of various solids could be made with the help of various transport reactions like halides, chalcogen halides, chalcogens, pnictides, etc. In order to proceed with CVT for the growth of BAs some prior basic understanding of the methods and thermodynamic background needed to avoid the unnecessary trials and errors. Here discussed some list of important parameters for CVT growth considerations.^{19,20}

- i. A suitable transport agent – To efficiently transport all the formed gaseous products, a transport agent needs to be chosen to transfer all components of the initial solid in to gas phase under chemical equilibrium.
- ii. Basic preconditions for CVT – The equilibrium position of the transport reaction needs to be balanced and reversible and not extreme, so that the transformation into vapor phase and the recrystallization in to solid phase may happen under a slightly changed environment. In theory, possibility of CVT reactions can be calculated thermodynamically with the parameters like Gibbs free energy ($\Delta_r G^0$) and equilibrium constant (K_p). In detail the reaction taken place and transport can

be expected only for $10^{-4} < K_p < 10^4$ and $-100 \text{ kJ mol}^{-1} < \Delta_r G^0 < 100 \text{ kJ mol}^{-1}$. The partial pressure acting as a driving force for the material transport between dissolution and deposition site separated by a temperature gradient. A highly endergonic reaction $\Delta_r G^0 > 100 \text{ kJ mol}^{-1}$ ($K_p < 10^{-4}$) results in the very low dissolution of solid transferring into gas phase, thus no transport take place. On the contrary, a highly exergonic reaction $\Delta_r G^0 < -100 \text{ kJ mol}^{-1}$ ($K_p > 10^4$) shows high dissolution of the solids in the source side, but very low possibility of the deposition of the solid in the growth side.

- iii. The suitable temperature – The temperature at $\Delta_r G^0_T = 0$ and $K_p = 1$ refers to as optimal for CVT growth. Optimal temperature $T_{opt} = \Delta_r H^0_T / \Delta_r S^0_T$ can be in the range of $\pm 100 \text{ K}$ for better growth. Temperature gradient is necessarily important to provide partial pressure gradient, which work as the driving force.
- iv. The transport direction – Transport is caused by different temperatures and then changed the equilibrium position. Based on Le Chatelier's principle the direction of the transport results from the sign of the reaction enthalpy. The exothermic transport reactions always transport towards the high temperature zone, while the endothermic transport reactions are towards the colder temperature zones.
- v. Mass transport rate – The CVT process can divide in to three steps, i.e., forward reaction of source material, gas motion and the reverse reaction leading to the recrystallization. The slowest among these is the gas motion and it determines the transport rate, which mainly taken place by diffusion or convection. The diffusion is highly affected when the total pressure is between 10^{-3} bar and 3 bar , while convection occurs at pressure higher than 3 bar .

1.3.4.2 Physical Vapor Transport

Evaporation or sublimation involves in the direct transport of materials from hot side to the cold side, either in vacuum environment or moving gas stream. In this method, seed crystals can be used to start nucleation, which can either be from the same material being grown or other material with similar lattice parameters. The source material evaporates and diffuses from hot end to the colder growth end and then nucleation starts in the seed positions.

1.4 Semiconductors

In semiconductors, electrical conductivity lies in between metals and insulators. Semiconductors are used in the manufacture of various electronics devices, including diodes, transistors and integrated circuits. As discrete components, semiconductors found use in LEDs, lasers, optical sensors, power devices, etc. The ability of handling wide range of current and voltage helps to integrate complex but vastly producible microelectronic devices. These are the key elements for majority of electronic devices and systems serving in signal processing, power electronics, computing, and communications.

1.4.1 Wide Bandgap Semiconductors

Wide band gap semiconductors (WBGs) are materials with relatively large band gap compared to conventional semiconductors used as infrared detectors and thermoelectrics. WBG semiconductor materials allow to produce much smaller, faster and reliable electronic devices with high performance and efficiency. Highly innovative materials with a wide bandgap include silicon Carbide (SiC) and gallium nitride (GaN), which are used as high-efficiency alternatives to commonly use silicon (Si). The large energy gap between the valence band and the conduction band of the WBG semiconductors translates to a higher

breakdown electric field, which provides the ability to operate in higher temperatures and lower vulnerability to radiation. Silicon with the bandgap of 1.12 eV, the threshold temperature required for the transition of electrons from valence band to the conduction band is around 150 °C.²¹ Therefore WBG semiconductors with larger band gap, can reach much higher temperatures without providing electrons to collect energy.

Furthermore, the WBGs like silicon carbide (SiC) and gallium nitride (GaN) have higher carrier mobility compared to silicon, which enables the use of WBGs in high speed computing and communication devices. Also, WBGs allow reduced energy consumption, lower on resistance, and higher breakdown voltages, which enables the use in micro scale devices to go even smaller in size and give more efficiency than the Silicon based semiconductors.

1.4.2 Wide Bandgap Semiconductors with High Thermal Conductivity

While using in high-temperature conditions, the reduction of heat dissipation is a very important factor to handle. So far Silicon Carbide (SiC) has the highest thermal conductivity among WBGs making it to use in high temperature applications, because of its capability to conduct heat and thereby increases the power density. Because of its high thermal conductivity and high melting point, SiC can operate at higher temperatures than industry leading Si. SiC has the highest thermal conductivity among other materials with the thermal conductivity range of 260-420 W m⁻¹ K⁻¹ at room temperature.²²

1.5 High Thermal Conductivity Materials

High heat loss and overheating in high-power-density functional units presents a major challenge in the modern electronic industry due to shrinking size and device density. As a

result of the heat generated in such devices, high temperatures limit device performance, reliability and also the lifetime of the device. Introducing high thermal conductivity materials as heat sinks for such devices is the most suitable solution for mobile and microelectronic devices. In modern day industry, there is a great desire to develop efficient and enhanced heat spreader for heat sinks which directly related to very high thermal conductivity. First, we are going to discuss about the traditional high thermal conductivity materials widely available.²³,

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1.5.1 Metals

In metals, the heat is mainly carried by electrons and are proportional to their electrical conductivities. Copper (Cu) and aluminum (Al) are the widely used heat sink materials in the industry with the room temperature thermal conductivities as high as $400 \text{ W m}^{-1} \text{ K}^{-1}$ and $240 \text{ W m}^{-1} \text{ K}^{-1}$ respectively. When it comes to shrinking size, microelectronic devices are looking for heat sinks and their supplementary parts to be electrically insulator or semiconductor to avoid unnecessary electrical contacts. While the metals are electrical conductors, the industry always uses an insulation layer between the electrical components and the metal heat sinks, which heavily reduces the heat transport due to low thermal conductivity in the insulation materials. Moreover, the metals thermal conductivity is determined by the electrons, which proportional to the temperature dependence of electrical conductivity, but also restricted by the electrical conductivity limits in high temperatures, researches are not able to do much enhancement to improve metal's thermal conductivities.

1.5.2 Traditional High Thermal Conductivity Materials

Carbon-based bulk materials like diamond and graphite, have been recognized as having very high thermal conductivities with room temperature values around $2000 \text{ W m}^{-1} \text{ K}^{-1}$. Compared to Cu these numbers are nearly four times higher, but such materials also suffer from their own disadvantages in the industry. Commonly accepted criteria to search for high thermal conductivity material is: ²⁵ 1) simple crystal structure, which leads to fewer number of atoms per unit cell; 2) low average atomic mass M_{ave} , which inversely proportional to κ of a material; 3) strong interatomic bonding, who increases the Debye temperature θ_D , which gives longer mean free path and average sound speed in the lattice; and 4) low anharmonicity, which reduces the phonon scattering effect in the crystal lattice. Based on this rule, with Group IV elements (mainly carbon and silicon-based structures) like diamond, graphite, carbon nanotubes and silicon have the highest thermal conductivity.²⁶ Group III-V compounds like boron nitride (BN) and aluminum nitride (AlN) and Group II-VI compounds like beryllium oxide (BeO) also conform to this rule and present relatively high thermal conductivity.²⁵

1.5.2.1 Diamond

Diamond is the most famous carbon structure with four electrons form covalent bonding to form a crystalline structure to have the highest thermal conductivity in nature. Diamond has a room temperature thermal conductivity record of more than $2000 \text{ W m}^{-1} \text{ K}^{-1}$. Low atomic mass, strong interatomic covalent bonding, cubic structure with symmetry, results in the high thermal conductivity of diamond. Also, these qualities enhance the physical properties of diamond like hardness, bulk modulus, and insulation properties.

However, both naturally grown and synthetic diamond growth require very high pressure and high temperature (HPHT) condition, which is very challenging to obtain in industry application due to high cost. The HPHT diamond synthesis with metal solvent catalysts is the presiding manufacturing process in the industry of blades and cutting applications. This process requires high temperatures over 2000 °C and high pressure in the range of 15-25 GPa, but the size of the growth is very limited.^{27, 28}

1.5.2.2 Graphite

Graphite, a hexagonal crystalline allotropic form of carbon sound as a mineral in nature, used as a solid lubricant, electrodes, batteries, solar panels and radiation heat sinks. Thermal conductivity of graphite is strongly influenced by its anisotropic nature, which comes from the honeycomb lattice with strong covalent bonding within the plane and weak van der Waals forces between planes. In-plane thermal conductivity at room temperature is near 400 W m⁻¹ K⁻¹, because of the rapid phonon propagation and out-of-plane weak bonding allows to separate the layers to make it electrically conductive. Also, graphite has one of the highest in-plane Young's moduli, but very low shear modulus in between layers. The large ratio between Young's modulus and the shear modulus makes the graphite use as solid lubricant and thus, is widely used in mechanical bearings and seals.²⁹

1.5.2.3 Carbon Nanotubes

Carbon nanotubes (CNTs) are cylindrical molecule structures that contain rolled-up sheets of mono-layer graphene. They can be categorized to single-walled carbon nanotubes (SWCNTs) with thermal conductivity of 2000 W m⁻¹ K⁻¹ and multi-walled carbon nanotubes (MWCNTs) with thermal conductivity of 3000 W m⁻¹ K⁻¹. Like diamond, heat is mainly

carried by phonons and active phonon modes, boundary scattering, phonon mean free path and Umklapp scattering processes are the parameters which determines the lattice thermal conductivity.³⁰⁻³²

The rolling-up direction of the atom arrangement in graphene layers and the tube dimensions are the determining factor of electrical and thermal properties. Apart from such thermal and electrical properties, CNTs also have unique mechanical properties that make them ideal candidates for electronic devices, electrochemical biosensors, batteries, cathode ray tubes (CRTs), etc. However, CNTS are still not developed as commercial heat sinks, because of the nanometer scale and due to the dependency of tube dimensions. CNTs are grown using chemical vapor deposition (CVD), which is still challenging to grow large scale and make structural damages during the acid treatment process to remove catalysts.

1.5.2.4 Boron Nitride

Other than this carbon based high thermal conductivity compounds, the mixture of Group III-V elements boron (B) and nitrogen (N), boron nitride (BN), has attracted many researches in the industry for decades due to its ultra-high thermal conductivity. The properties of hexagonal boron nitride (h-BN) are very much similar to graphite, while cubic boron nitride (c-BN) is similar to diamond. Recently, researchers found out room temperature thermal conductivity of c-BN is close to $1600 \text{ W m}^{-1} \text{ K}^{-1}$, only in isotopically pure boron environment.³³ But due to the requirement of extreme temperature and pressure conditions of the growth process, high cost and also because of the large bandgap, it is quiet challenging to use in semiconductor industry applications.

1.5.3 New Criteria to Define High Thermal Conductivity

Only few materials can be identified with the traditional criteria to define high thermal conductivity. Studying new materials with high thermal conductivity is limited due to the difficulties in phonon analysis. It becomes further challenging to calculate thermal conductivity when 4-phonon processes are considered with introducing impurities. In 2013, Lindsay *et al.* made remarkable discovery of new materials with ultra-high thermal conductivity with first principle calculations.^{1, 34} Predicted results show high thermal conductivity in boron-based Group III-V compounds like boron arsenide (BAs), boron nitride (BN), boron phosphide (BP) and boron antimonide (BSb). Among these boron-based compounds, BAs has an exceptionally high room temperature thermal conductivity of $2000 \text{ W m}^{-1} \text{ K}^{-1}$, which is comparable to diamond (Shown in Figure 1.2). This result is heavily differed from the room temperature thermal conductivity calculated from common criteria only around $200 \text{ W m}^{-1} \text{ K}^{-1}$.²⁵ Measured values from Figure 1.2 for diamond (open black squares³⁵, triangles³⁶, circles³⁷, and crosses³⁸) and BP (open purple circles²⁵ and squares³⁹) are given. Also shown are RT ($T = 300 \text{ K}$) values (solid black circles) for common high materials⁴⁰⁻⁴²: gallium nitride ($230 \text{ W m}^{-1} \text{ K}^{-1}$), aluminum ($240 \text{ W m}^{-1} \text{ K}^{-1}$), aluminum nitride ($285 \text{ W m}^{-1} \text{ K}^{-1}$), copper ($400 \text{ W m}^{-1} \text{ K}^{-1}$), and silicon carbide ($490 \text{ W m}^{-1} \text{ K}^{-1}$).

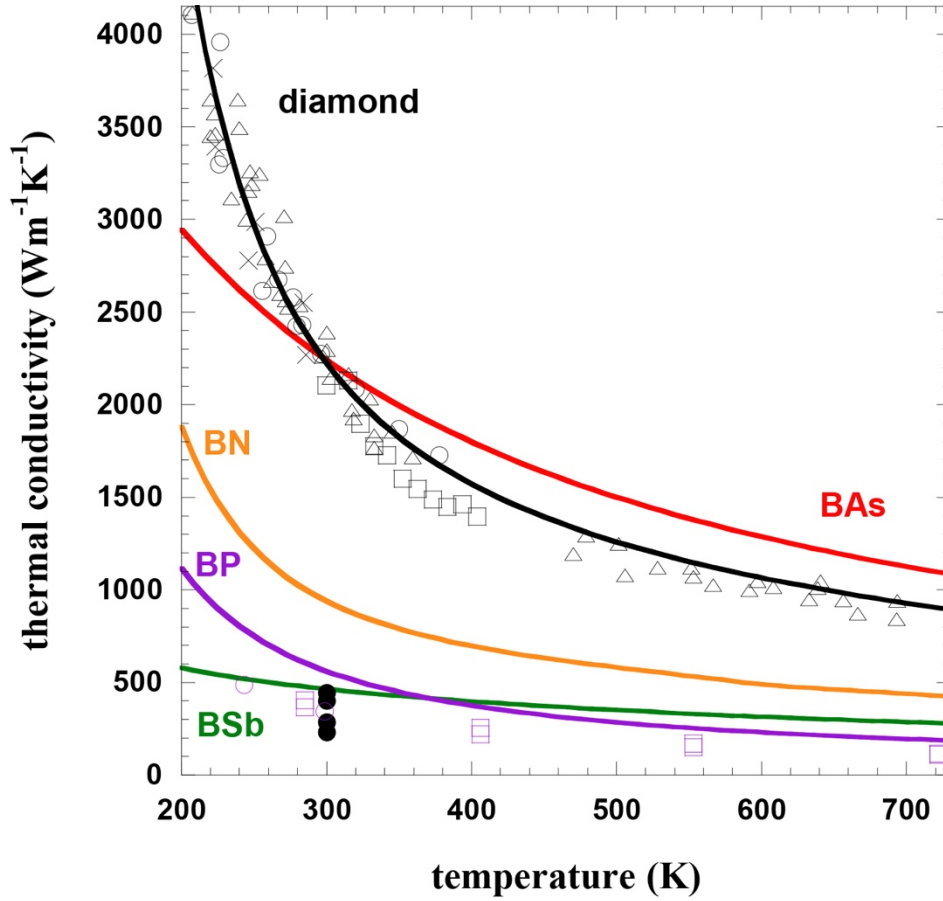


Figure 1.2 Calculated κ_{nat} vs temperature for cubic BN (orange), BP (purple), BAs (red), BSb (green), and diamond (black).¹

1.5.4 Identify New Materials with High Thermal Conductivity

These unusual thermal conductivities arise from the phonon properties of BAs, including large frequency gap between the acoustic and optic phonons (a-o gap) given by the large atomic mass ratios of the component elements (Figure 1.3). At the same time, the bunching of the acoustic phonon bands in BAs also reduces the a-a scattering give rise to κ . Since the isotopically pure heavy atom arsenic (As) mainly dominates in the phonon region, it also gives very weak phonon-isotope scattering. Figure 1.3 shows the comparison of phonon properties of BAs and Si. BAs has a large *a-o* frequency gap, which is absent in Si. Note that the near-zone center acoustic velocities for BAs and Si are similar. However, the three

acoustic branches [two transverse (TA_1 and TA_2) and one longitudinal (LA)] are bunched closer to one another in BAs than are the corresponding branches in Si.

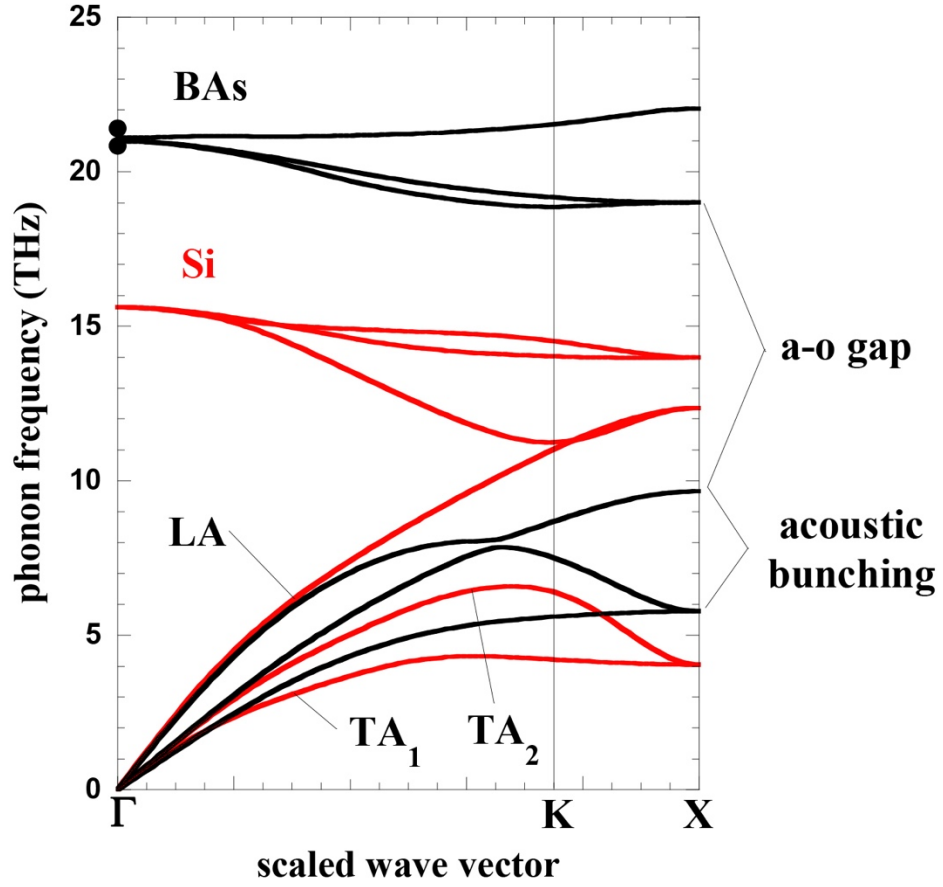


Figure 1.3 Phonon frequency vs scaled wave vector in the high symmetry $\Gamma \rightarrow K \rightarrow X$ direction for BAs (black) and Si (red) with experimental Raman data for BAs (black circles)⁴³.

All these calculations made assuming the three-phonon scattering processes govern the thermal transport of such materials. However, including the four-phonon processes and phonon-impurity scattering, Feng *et al.* made new calculations showing that predicted thermal conductivity of BAs can be reduced from $2000 \text{ W m}^{-1} \text{ K}^{-1}$ to $1400 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature.⁴⁴ Intrinsic phonon scattering is mainly caused by lattice anharmonicity and first-order anharmonic couplings involve only three phonons.⁴⁵ In addition to that second order

anharmonicity gives rise to the four-phonon processes and researchers found that four-phonon scattering is quite strong in BAs, than the three-phonon scattering for many frequencies. As shown in Figure 1.4, the number of three phonon scattering is heavily restricted by a large acoustic-optical (a-o) energy gap, however does not prevent four-phonon processes between acoustic and optical phonons. Blue ovals indicate the regions where four-phonon scattering plays an important role. Green ovals in the Figure 1.4 insets indicate that our four-phonon results reproduce well the universal law $\lim_{\omega \rightarrow 0} \tau^{-1} = 0$, which is a critical mark of the calculation accuracy. Therefore, the relaxation time of phonons are heavily reduced and increases the scattering rates which reduces the lattice thermal conductivity.

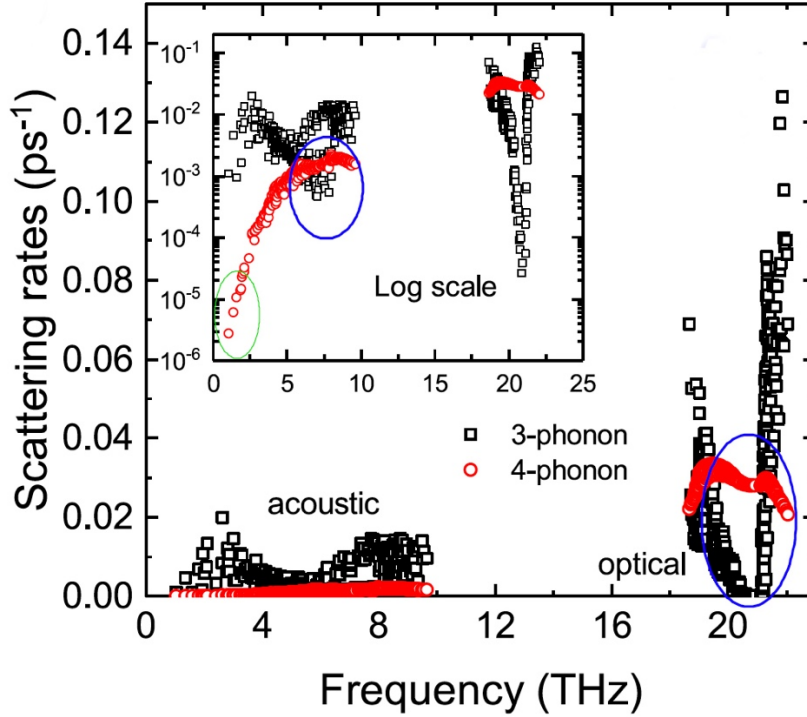


Figure 1.4 First-principles three-phonon (black dots) and four-phonon (red dots) scattering rates of BAs at 300 K. The insets are in log-linear scales to give a better view of the low-frequency regions.⁴⁴

Even though the intrinsic thermal conductivity of BAs reduces by the effect of four-phonon scattering, it is still higher than all the industry leading metals and wide bandgap semiconductor materials. At the same time based on first principle calculations, studies of electrical properties of BAs carried out and Liu *et al.* reported that BAs also have simultaneously high hole mobility ($2110 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and electron mobility ($1400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) at room temperature.⁴⁶

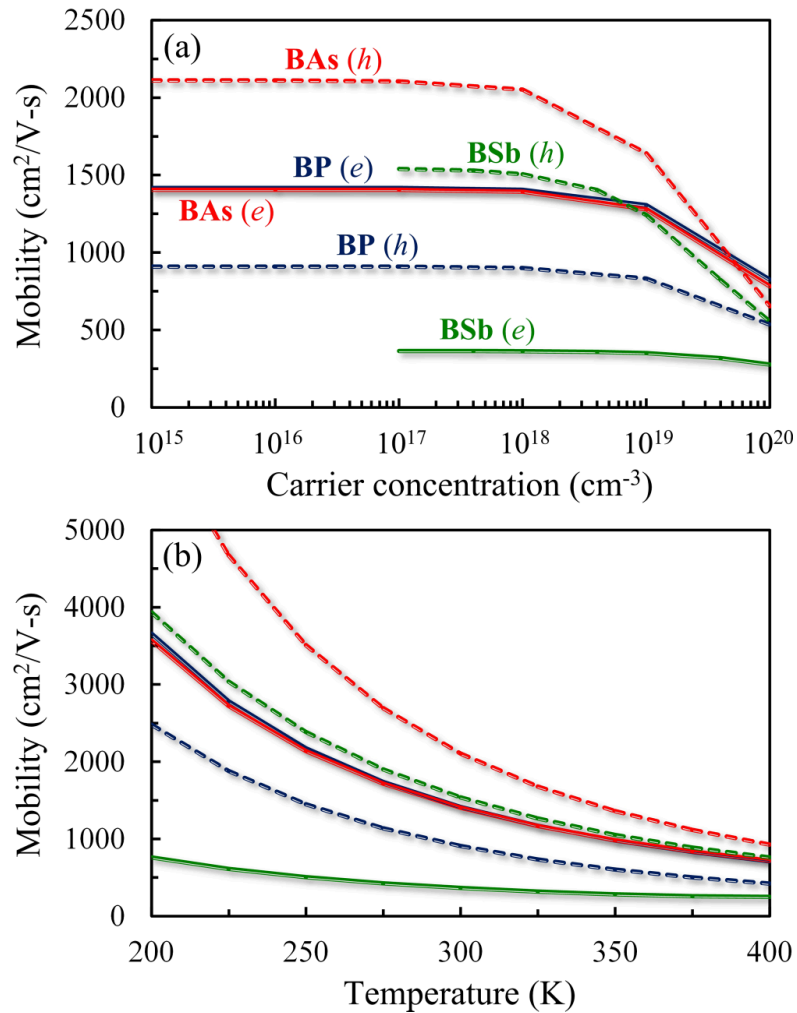


Figure 1.5 Carrier mobilities of BP BP (blue), BAs (red), and BSb (green) with varying (a) carrier concentrations and (b) temperatures. The dashed and solid lines represent the mobilities of holes and electrons, respectively.⁴⁶

Having high mobility in both p-type and n-type is unusual since most common group IV and III-V semiconductors exhibit high mobility only for one type of carrier. This comparable mobilities occur due to the very small difference in the effective mass of electrons and holes in BAs compared to other group III-V semiconductors.

1.6 Outline and Objective of this Work

The major goal of my research is to grow BAs single crystals with high thermal conductivity and enhance its electrical and thermal properties. Based on theoretical calculations and computer simulations, I synthesized BAs single crystals with thermal conductivity and carrier mobility close to predicted values. To achieve this objective BAs single crystals needs to be synthesized first and optimized the growth parameters by introducing new techniques. I studied the use of different boron sources to increase the reaction rate and improve the quality of as-grown BAs crystals. At the same time, I introduced different nucleation sites to grow BAs using CVT and obtained high thermal conductivity and electrical conductivity. After successfully grew BAs crystals with large size and quality, characterizations and measurements of electrical, thermal and optical properties, including thermal conductivity are performed on these for detailed analysis.

In this dissertation, a brief introduction to high thermal conductivity materials, the purpose of having high thermal conductivity materials in device applications and single crystal growth techniques are first presented. Then the characterization of BAs and electrical and thermal measurements are presented in the following chapter. Next chapter focuses on BAs single crystal growth using enhanced CVT techniques like the use of different boron sources, different nucleation sites and optimal growth parameters, etc. At last the dissertation ends with summary and my future plans on BAs.

CHAPTER 2 CHARACTERIZATION TECHNIQUES

Quantitative and qualitative analysis of single crystal's is challenging due to certain parameters like the size, purity and uniformity. Due to the challenges of growing high quality and larger size, some measurements are limited or ends up with major uncertainty of the outcome due to the smaller size of the crystals. To overcome these problems, choosing suitable techniques, especially on thermal and electrical transport measurements are important factor to figure out the basic properties of the material.

2.1 Hall Measurement

The Hall effect was discovered by Edwin Hall in 1879. It is the production of a voltage difference so called Hall voltage produced by charge carriers under applied magnetic field. If charge carriers (holes or electrons) move or an electrical current flow across electrical conductor under magnetic field, the magnetic field produce a transverse force (Lorentz force) on the moving charge carriers, which results in accumulation of charges and generate electric field (ε), as shown in Figure 2.1.⁴⁷ Hall voltage (V_H) is the voltage difference caused by this electric field of the accumulated charge carriers.

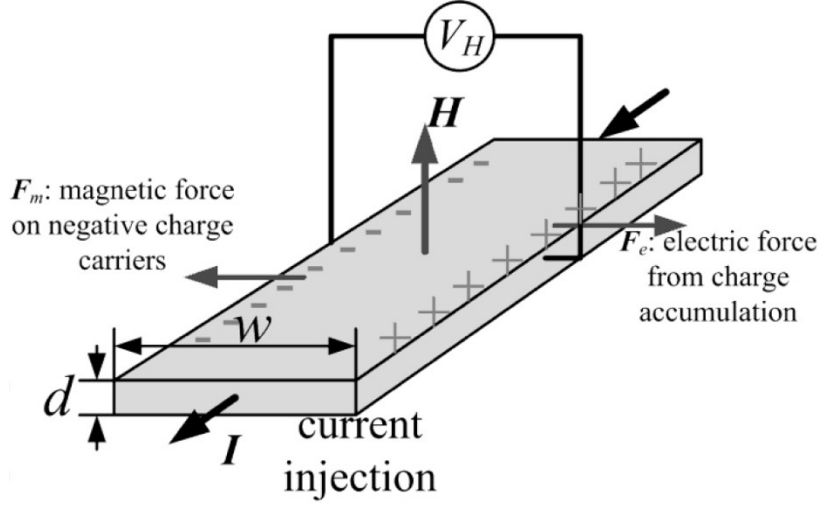


Figure 2.1 Schematic design of Hall measurement.⁴⁷

Based on this, Hall measurements are designed to measure various electrical transport properties like carrier concentration and mobility. With the use of rectangular sample with the dimensions parallel to the current directions are l , w and t , respectively. For conductive rectangular shape sample in a perpendicular magnetic field B , the carrier concentration is given by:

$$n_H = \frac{1}{R_H q}$$

Where q is the charge of the carrier (electrons or holes) and R_H is the Hall coefficient given by:

$$R_H = \frac{V_H t}{IB}$$

From the use of electrical resistivity and carrier concentration, we can obtain the carrier mobility:

$$\mu = \frac{1}{\rho q n_H}$$

To obtain high carrier mobility in BAs, this measurement is important to perform in all the crystals after the enhancement made in the growth process. With irregular shapes and different thickness, it is very challenging to obtain accurate results. Therefore, we used Physical Property Measurement System (PPMS by Quantum Design, Inc) to measure most of the transport properties under different temperatures.

2.2 Electrical Resistivity Measurement

Electrical resistivity usually depends on electrical conductivity measurement, which is inversely proportional to the resistivity. The main method to measure resistivity is to use the four-probe method, also gives accurate results with minimal error. Figure 2.2 shows a schematic diagram of this four-probe method with current and voltage flow.⁴⁸ Applied electrical current flows through the conducting sample via the outer probe 1 & 4, and the voltage is measured with respect to current via inner probe 2 & 3. Due to the high electrical impedance no current flows through the inner voltage probes. The resistance of the sample can be calculated from the slope of V-I curve, and the resistivity ρ can be calculated by equation $\rho = R \frac{A}{L}$, where R is the calculated resistance from Ohm's law, A is the cross-sectional area and L is the distance between two voltage probes.

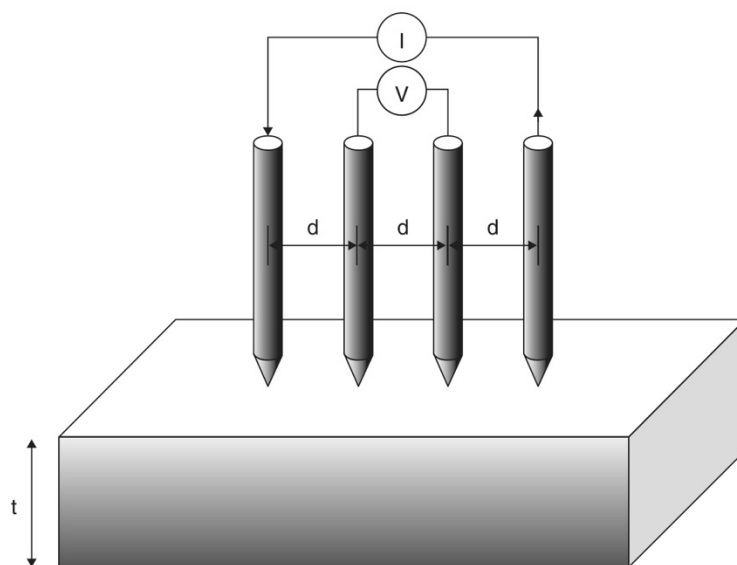


Figure 2.2 Schematic diagram of four-probe method for electrical transport measurement.⁴⁸

For the single crystals with smaller size (< 1 mm), it's very challenging to attach the probes with maintaining the proper distance and without spreading the attaching agents like silver paint or epoxy. This resistivity measurement over different temperatures is helpful to identify the metallic or semiconductor nature of the conductive crystals. For smaller samples which are thinner than 40% of the probe length, current path gets limited and resulted in overestimated resistance. To avoid that issue, geometric correction factors need to be introduced to the calculation.

2.3 Optical Measurement

Optical absorption spectroscopy is an important analytical technique used to understand the degree of absorbance or reflectance of incident electromagnetic (EM) radiation by sample within the ultraviolet to visible range. Photons within the UV-Vis spectrum possesses the energy required to excite and produce energy state transitions in the electrons in the sample lattice. In this dissertation, UV-Vis is used to determine the direct and indirect

bandgap of a semiconductor material BAs using both transmittance and reflectance measurements. Using commercial Ultraviolet-Visible (UV-Vis) NIR spectrophotometer, we can perform transmittance (T) and reflectance (R) measurements to find the absorption coefficient (α) to calculate the direct and indirect optical band gaps. The second approach is the use of spectroscopic ellipsometry, can measure the ellipsometry angles ψ and Δ in the wavelength range of 190 nm to 1000 nm to calculate the refractive index and the extinction coefficient of the samples, which gives the absorption coefficient.

To measure the absorption coefficient α , first need the transmittance and reflectance data for both UV and visible range. The α can be expressed as:⁴⁹

$$\alpha = \frac{1}{d} \ln \frac{(1 - R)^2}{T}$$

Where d is the sample thickness, R is the percentage reflectance and T is the percentage transmittance. By plotting the measured absorption coefficient as a function of photon energy can expressed in two ways. The absorption coefficient associated with the indirect bandgap can be given by:⁵⁰ $\alpha = A(h\nu - E_{gi})^2$ where the $h\nu$ and E_{gi} are the photon energy and the indirect band gap, respectively. In the other way, the associated with direct bandgap transition can be given by:⁵¹ $\alpha^2 = B(h\nu - E_{gd})$ where E_{gd} is the direct bandgap of the substances.

Measurement principle of ellipsometry starts with the ratio r between the complex Fresnel reflection coefficients for p - and s -polarized light (r_p and r_s) with wavelength l , is given by:

$$\rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta}$$

Where ψ and Δ are the ellipsometry angles with $\tan \psi$ capturing the amplitude ratio while Δ the phase difference. For a bulk, transparent sample, the dielectric function ε can be expressed as:⁵²

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = \sin^2 \phi \left[1 + \left(\frac{1 - \rho}{1 + \rho} \right)^2 \tan^2 \phi \right]$$

Where ε_1 and ε_2 are the real and imaginary part of ε , respectively and ϕ is the incident angle. ε_1 and ε_2 are simultaneously obtained if the angles ψ and Δ can be accurately measured. In addition, the complex refractive index n is calculated by:

$$n = n + ik = \sqrt{\varepsilon}$$

Where n and k are the refractive index and extinction coefficient, respectively. With the use of n and k , the absorption coefficient $\alpha = 4\pi k/\lambda$ can be obtained.⁵

By plotting (Tauc plot) the square root of α with respect to photon energy, the linear portion that intersect with the x-axis is just the energy of the indirect bandgap E_{gi} and similarly plotting the square of α over the photon energy, where the linear portion intersect with the x-axis is the energy of the direct bandgap E_{gd} .⁵³ For opaque and very thin BAs samples, we used both these techniques to measure the indirect and direct band gaps, which shows proper agreement with the calculated results.

2.4 Heat capacity Measurement

The heat capacity (C_p) of solids is can provide important information about the lattice, electronic and magnetic properties of the materials. It also helps to analyze the thermodynamic nature of a given material. In order to calculate the enthalpy ($H(T)$), entropy ($S(T)$) and Gibbs free energy ($G(T)$) of a material temperature dependent C_p data are required.

C_p at constant pressure is defined as: $C_p = (dQ/dT)_p$, where Q is the heat and temperature dependence C_p can be fit to a polynomial equation:⁵⁴

$$C_p = aT^2 + bT + cT^{-0.5} + d$$

Using the resulted coefficients, we can calculate the following thermodynamic parameters:

$$H(T) = H_f(298) + \int_{298}^T C_p dT$$

$$S(T) = S_f(298) + \int_{298}^T \frac{C_p}{T} dT$$

$$G(T) = H(T) - T S(T)$$

To measure the C_p , Dynacool Physical Property Measurement System (PPMS) from Quantum Design, Inc. is used in the temperature range of 2.0 K to 380 K and Figure 2.3 shows the sample attachment to the platform in PPMS heat capacity option.

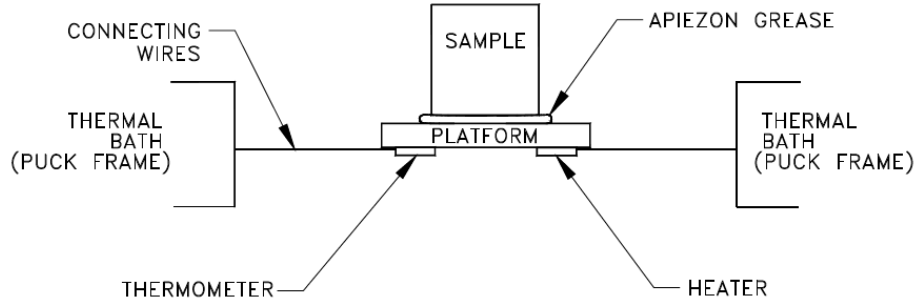


Figure 2.3 Thermal connections to sample and sample platform in PPMS heat capacity option.

2.5 Thermal Conductivity Measurement

Thermal conductivity (κ) measurement is the most important part of this project. Even though a lots of thermal conductivity measurement techniques are available, such traditional

methods like laser flash method⁵⁵ and 3ω -method⁵⁶ are not suitable enough for small scale single crystal measurements. When performing thermal measurements on millimeter or micrometer scale samples, getting proper temperature readings at different locations become challenging. When it comes to materials with high κ this issue becomes even worse, because in a short distance leads to a very small temperature deviation, comparable to the error itself, which makes the data completely unreliable. Therefore, new techniques like pulse and probe lasers designed for high κ materials with millimeter or even smaller in size are used for this project.

2.5.1 Time Domain Thermoreflectance Method

Over the past two decades, ultrafast laser-based transient thermoreflectance (TTR) methods is an efficient and reliable technique for characterizing thermal properties of both thin films and bulk materials. In particular, time domain thermoreflectance (TDTR) method has been widely used to measure thermal conductivity of thin films and bulk materials with ranging from a high end at $\sim 2000 \text{ W m}^{-1} \text{ K}^{-1}$ to as low as $0.03 \text{ W m}^{-1} \text{ K}^{-1}$.⁵⁷ TDTR is one of the verified techniques to measure thermal conductivity in millimeter or micrometer scale samples, where traditional methods cannot be applied due to the non-zero temperature difference of a short length in a small sample.^{58, 59} Figure 2.4 shows the schematic of a typical transient thermoreflectance setup. This method is contrast from the optical pump-probe technique, in which a pump pulse is used to excite the sample, changing the optical properties, and a second timed delayed probe pulse measures the change, as shown in Figure 2.5.⁴ The change has direct relationship with the thermoreflectance coefficient of a thin top layer of metal. This high-resolution technique makes it well matched to the study of a wide range of transport processes occurring on time scales from femtoseconds to nanoseconds range.

Usually, the κ can be calculated from the data fitted in to a numerical model. Note that the diamond sample from Figure 2.5 has the natural carbon abundance (1.1% ^{13}C) and a low level of boron (< 0.05 ppm) and nitrogen (< 1 ppm) impurities. The 300 K data shown in Figure 2.5 are averaged over 200 and 140 runs at the same location for diamond and BAs, respectively. The data for BAs at higher temperatures are averages of about 10 runs and show slightly increased noise.

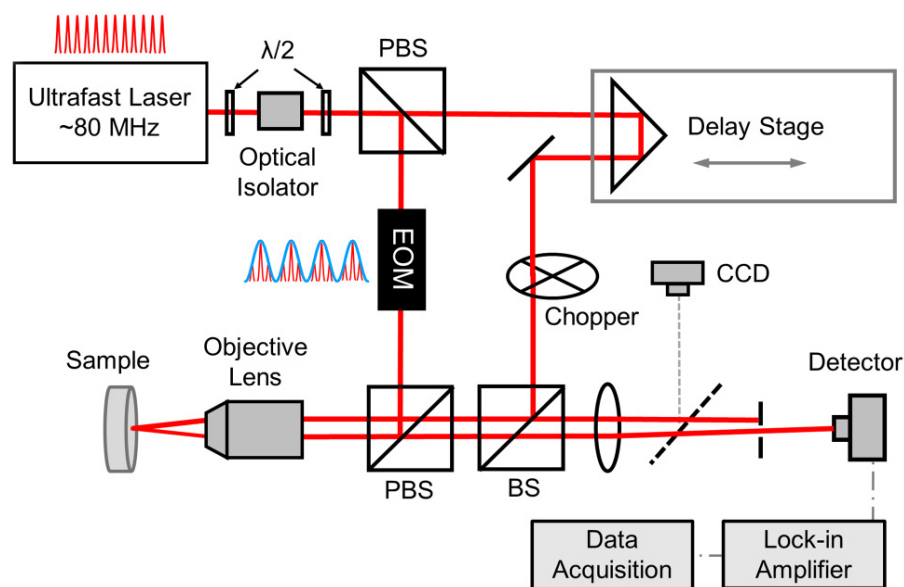


Figure 2.4 Schematic of a typical transient thermoreflectance setup. The acronyms PBS, BS, EOM and $\lambda/2$ stand for polarizing beam splitter, beam splitter, electro-optic modulator and half-wave plate, respectively.⁵⁷

The common TDTR uses a Ti:sapphire laser oscillator as the laser source. The laser oscillator produces continuous sub-picosecond optical pulses at a higher frequency rate around 80 MHz. The output divide into two paths, a pump and a probe path, a pump path includes an optical delay line and an electro-optic modulator capable of chopping the pump beam at frequencies beyond 10 MHz. The probe path typically includes an audio-frequency mechanical chopper to facilitate the removal of coherent background signals. The term “thermoreflectance” refers to the fact that the probe measures changes in the temperature of

the sample through the dependence of the optical reflectivity R of a metal film transducer on temperature, T ; dR/dT is the coefficient of thermorefectance. An Aluminum (Al) thin film has an unusually large thermorefectance at probe wavelengths generated by lasers, $dR/dT = 10^{-4} K^{-1}$ near room temperature at wavelengths near 800 nm. This matter, combined with the strong sensitivity of Al reflectivity to strain, makes Al ideally suited for both TDTR and picosecond acoustics.⁶⁰

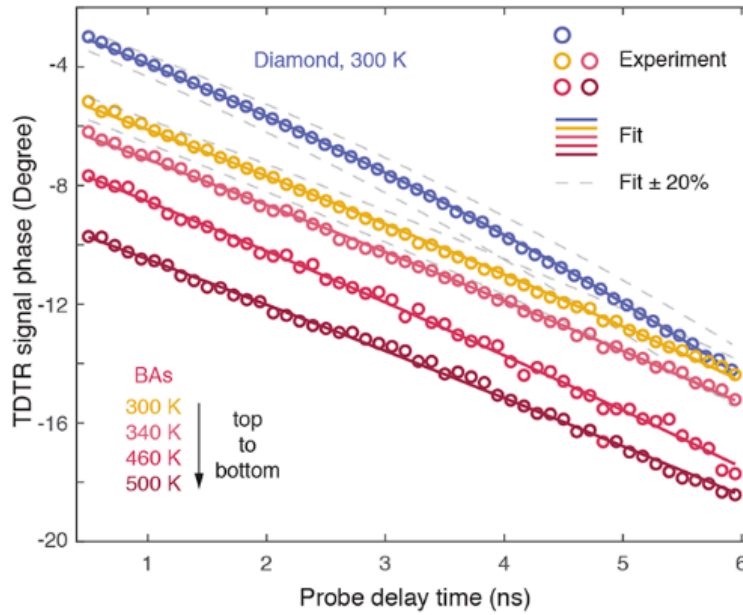


Figure 2.5 Representative TDTR phase signals and the best fitted curves for a diamond crystal acquired from Element Six and a BAS crystal at different temperatures.⁴

The κ value can be determined by using the TDTR data. A lock-in amplifier uses to measure the fundamental component of the probe signal at the modulation frequency ω_o and all other background harmonics are removed. The output will be the amplitude A and phase ϕ of the fundamental component of the probe signal with respect to the reference wave at every delay time τ . Mathematically, the solution takes the form of a “transfer function,” a complex

number $Z(\omega_o)$ such that the output of the lock-in amplifier for a reference wave $e^{i\omega_o t}$ is given by:

$$Ae^{i(\omega_o t + \phi)} = Z(\omega_o)e^{i\omega_o t}$$

According to this transfer function under the simplified assumption that the response of the sample to the laser input is both linear and time invariant (LTI), we can use all the mathematical tools available for LTI systems, such as superposition, convolution and simple conversion between the time and the frequency domains. Then to analyze the heat transfer, if the LTI system's exponential decay replaced with the experimental thermal response of a multilayered sample heated and probed by Gaussian laser spots, including both the cross-plane and in-plane thermal conductivities of each layer, thermal conductivity σ can be determined. Thermal conduction through layered structures in isotropic media has been described in several places,^{61, 62} and Cahill *et al.*⁵⁹ gave a specific solution for TTR. Here we adopt the approach described by Carslaw & Jaeger *et al.*⁶² for one dimensional conduction and extend it to account for radial, anisotropic effects using a Hankel transformation.⁶³

For a single slab material in the frequency domain, the temperature θ_t and heat flux f_t on the top side of the slab are related to the temperature θ_b and the heat flux f_b on the bottom side through:

$$\begin{bmatrix} \theta_b \\ f_b \end{bmatrix} = \begin{bmatrix} \cosh(qd) & \frac{-1}{\sigma_z d} \sinh(qd) \\ -\sigma_z \sinh(qd) & \cosh(qd) \end{bmatrix} \begin{bmatrix} \theta_t \\ f_t \end{bmatrix}$$

Here d is the layer thickness, σ_z the cross -plane thermal conductivity and $q^2 = i\omega/\alpha$, where α is the thermal diffusivity. Multiple layers are handled by multiplying the matrices for individual layers together,

$$\begin{bmatrix} \theta_b \\ f_b \end{bmatrix} = \mathbf{M}_n \mathbf{M}_{n-1} \dots \mathbf{M}_1 = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} \theta_t \\ f_t \end{bmatrix}$$

Here $\mathbf{M}_n$ is the matrix for the bottom layer. An interface conductance G is treated by taking the limit as the heat capacity of a layer approaches zero and choosing σ_z and d such that $G = \sigma_z/d$. If the bottom surface of the n^{th} layer is assumed to be adiabatic, or if the n^{th} layer is treated as semi-infinite, then in both cases the above equation reduces to $C\theta_t + Df_t = 0$ and the surface temperature will give by:

$$\theta_t = \frac{-D}{C} f_t$$

Where f_t is the heat flux boundary condition applied to the top surface. In the majority of this experiments, the semi-infinite boundary condition is an accurate description of the physical situation.⁵⁸

In the measurement of BAs samples, a set of TDTR measurements was taken on Al-coated BAs samples where the diameter ($1/e^2$) of the pump and probe laser spots are 58 μm and 9 μm , respectively. Pump intensity modulated by an electro optic modulator (EOM) at 3 MHz frequency. An 82 nm thick Al coating deposited on to the top surface of each BAs single crystal.⁶⁴ As shown in the Figure 2.5, κ values for each sample measured on many spots and measured the thermoreflectance curves for each spot and found out the highest and lowest room temperature thermal conductivities were $1160 \pm 130 \text{ W m}^{-1} \text{ K}^{-1}$ and $640 \pm 70 \text{ W m}^{-1} \text{ K}^{-1}$, respectively.⁴

2.5.2 Steady State Method

In order to measure the bulk thermal conductivity of BAs, this steady state method is developed with the use of Silicon (Si) sample as the reference. A bar-shaped BAs sample is cut from as-grown BAs crystals and joined using epoxy to the Si bar sample with the known thermal conductivity. These two pieces are suspended and placed between a resistive heater

and a heat sink as shown in Figure 2.6. The differential thermocouple made of a constantan wire connected with two copper wires at the two ends, with a diameter of $12.7\ \mu\text{m}$ for all the wires. The thermocouple junctions anchored on the sample surface using superglue, with the lead wires suspended in vacuum. The sample is enclosed by a Copper radiation shield and placed in a cryostat that is evacuated to about 1×10^{-6} torr by a turbomolecular pump. At each environment temperature, the temperature drops along the Si reference and the BAs sample are measured by the two differential thermocouples at different heating powers, where the slopes of the linear fitting were used to calculate the ratio in the temperature gradient between the sample and the reference and obtain the sample thermal conductivity.⁴

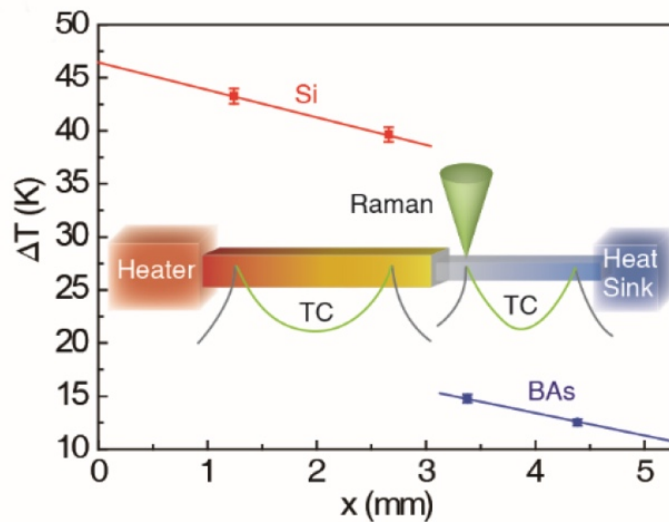


Figure 2.6 Schematic showing the suspended BAs and Si bars for the steady state thermal conductivity measurement.⁴

2.5.3 Time Domain Photoluminescence Method

Photoluminescence mapping (PL-mapping) and time-domain thermophotoluminescence (TDTP) are two optical measurement techniques that develop to provide rapid and non-destructive characterization of thermal conductivity with shorter period of time and with small sample preparation.⁶⁵ PL-mapping provides real-time image of crystal quality

and the κ measurement over mm-sized crystal surfaces, while TDTP uses a local spot on the sample surface and measure its κ using nanosecond laser pulses. These new techniques reveal that the apparent single crystals are not only nonuniform in κ but also are made of domains of very distinct κ . Because PL-mapping and TDTP are based on the band-edge PL and its dependence on temperature, they can be applied to other semiconductors, thus allows to identify the uniformity of κ value and the quality by rapid screening the BAs for future device applications.

Based on the relationship of PL with crystal quality and temperature, we develop and demonstrate two new optical techniques that can produce rapid non-intrusive imaging of κ over a large region with micrometer spatial resolution with little sample preparation: photoluminescence mapping (PL-mapping) and time-domain thermophotoluminescence (TDTP). PL-mapping can generate 2D images of κ within seconds and even in real-time. TDTP uses two pump-pulse nanosecond lasers to determine κ from an arbitrary spot of a sample surface. Because PL-mapping and TDTP use simple lasers, they are accessible by many researchers, thus will greatly accelerate the pace of discovery, development, and applications of semiconductor-based high κ materials.

To obtain a quantitative κ and experimentally verify the relationship between PL-mapping and κ value, we developed an optical setup requires no sample preparation. Figure 2.7 shows the schematic design of the TDTP setup.⁶⁵ In comparison to TDTR, TDTP uses a pump pulse (527 nm, 140 ns) to generate the localized heat in a sample, and a weak time-delayed probe pulse (527 nm, 100 ns) to collect the temperature and heat transfer throughout the sample. κ is obtained by fitting the temperature data to known numerical solutions. Instead of ultrafast femtosecond or picosecond lasers that used in TDTR, TDTP uses cost

relate to the magnetic susceptibility (χ), where the sign determines the samples diamagnetic or paramagnetic behavior, while the hysteresis loop determines the ferromagnetic behavior.

2.7 Structure Characterization

2.7.1 X-ray Diffraction Spectroscopy

X-ray diffraction (XRD) is a rapid analytical technique used to determine the crystallographic phase structure and can provide information on unit cell dimensions. XRD spectra analysis of single crystal BAs samples were conducted on a Rigaku Smartlab multipurpose diffractometer with an X'celerator detector (Rigaku Smartlab X-Ray Diffractometer, Cu K α radiation source).

2.7.2 Scanning Electron Spectroscopy & Energy Dispersive X-ray Spectroscopy

BAs single crystals were characterized by scanning electron microscopy (SEM Leo 1525 Gemini FEG, Zeiss and FE-SEM, LEO 1525) and the elemental composition was investigated with energy dispersive x-ray spectroscopy (EDS). EDS detector measures the energy of the emitted photons in the X-ray electromagnetic spectrum. The detected X-rays are divided in to energy channels based on their interaction with the detector and generate an energy spectrum. This spectrum helps to determine the elements corresponding to each energy peak, where this combined with the SEM images to form EDS mapping of data to present the elemental analysis over a defined area of the sample.

2.8 Raman Spectroscopy

Raman spectra was used to identify the phonon dynamics of BAs samples with natural isotopic abundant and also isotopically pure boron content. The Raman spectra of BAs

samples were measured using a Horiba JYT64000 triple spectrometer excited by a 632 nm laser at 294 K.⁶⁶ The spectra were collected in a backscattering setup with incident and scattering light propagating normal to the sample surface. The unpolarized Raman spectra gives an average of two spectra taken at the same spot of the given sample, one is parallel and the other one is crossed incident and scattered light polarizations. Raman scattering from phonons is a two-photon process in which incoming laser light excites electrons in the material, which in turn results in emission or absorption of phonons via electron-phonon coupling. Laser excitations can also produce Raman scattering from electronic excitations, known as electronic Raman scattering (ERS).⁶⁴ ERS observed in some of the BAs samples due to high hole concentration.

CHAPTER 3 SYNTHESIS OF BORON ARSENIDE CRYSTALS

In 2013, Lindsay et al. made the first principle calculations on the high thermal conductivity of Group III-V binary compounds, which makes a rapid acceleration in the research world to work on high κ materials like BAs, BN and BP. Based on the predictions on both thermal and electrical properties, BAs has to have both high thermal conductivity close to $1400 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature,⁴⁴ which only seconds to diamond and impressive semiconductor properties with wide bandgap and high carrier mobility. Even though research on BAs has recently been revived due to the high thermal conductivity, BAs growth techniques and mechanisms are still in a primitive stage, further process optimizations are needed to grow large size BAs single crystals of high quality. Recently, BAs has been confirmed to have an indirect bandgap of $1.9 - 2.0 \text{ eV}$ ⁵ at room temperature and so far, BAs is the only known wide bandgap semiconductor which has ultra-high thermal conductivity. The only known way to grow BAs SCs thus far is chemical vapor transport (CVT) inside a sealed quartz tube, which was first achieved by Chu and Hyslop in 1972,⁶⁷ although the first report of polycrystalline BAs by Perri was in 1958.⁶⁸ Recently, many efforts to optimize this CVT process has been made by multiple groups in order to enlarge the size and to enhance their quality to achieve high κ value.^{2, 3, 69, 70}

In 2018, the maximum room temperature κ value obtained from BAs increased to near $1100 \text{ W m}^{-1} \text{ K}^{-1}$.⁴ However, due to completely different chemical properties between elemental B and As and the extreme danger of the elemental sources, the growth of BAs become very challenging. The major challenges of the growth of BAs include the high chemical stability and the high melting point of boron (B), which is over 2000°C and the toxicity of arsenic (As), which can directly sublime from solid to the gas phase at 615°C

under atmospheric pressure. Therefore, using the vapor phase of arsenic at a high temperature can make heavily toxic compounds like arsenic oxide (As_2O_3) during the growth process. In order to prevent that, BAs growth process needs to be done in a closed system, capable of handling high vapor pressure generate from As at higher temperatures. Growth temperature is limited due to the decomposition of BAs into B_{12}As_2 above 920 °C, which is way below the melting temperature of B.³ All these factors led to slow progress on BAs growth and understanding the basics of chemical parameters to improve the quality of BAs. Here in this project, we focused on two growth mechanisms to synthesize BAs single crystals. At the same time, we put more efforts to improve the most attractive features like thermal and electrical properties by enhancing the growth process.

3.1 BAs Synthesis from Direct Reactions

By looking at the As-B binary phase diagram in Figure 3.1,⁷¹ two phases of compounds exist, BAs and B_{12}As_2 . Even though the As-B phase diagram shows BAs decompose to B_{12}As_2 at 1070 °C, experimentally it has been proven that it begins at 920 °C.⁶⁸ Considering the melting point of B (~2027 °C) and the decomposition temperature, it looks difficult to get BAs phase via commonly used melting method.

BAs phase can be simply achieved by the direct reaction of B powders with As chunks at above 800 °C.^{2, 3, 67} Since the direct reaction of B and As is very slow, B and As are placed in a sealed quartz ampoule and heated in a furnace for 48 - 72 hrs., and obtained black powders, which is clearly proven to be BAs from X-ray diffraction (XRD) and some As residues. By collecting these BAs powders or chunks and making them into thin powders using a ball milling machine and repeating this process 4 - 5 times with adding excess As, can

easily see that the amount of BAs increases in each repeating step. That means excess As continues to react and fill out the As vacancies in BAs powders.

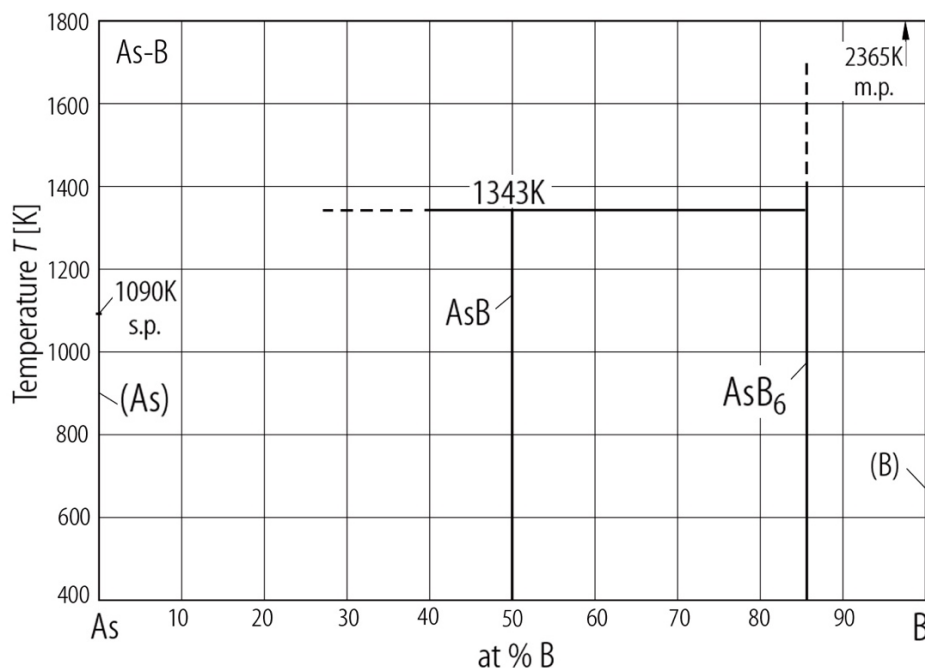


Figure 3.1 As-B partial phase diagram.⁷¹

However, this method is not suitable to grow large size BAs single crystals for further studies and κ measurements. During the ball milling process and from the precursors itself can add some impurities that directly introduced into the lattice of as-grown BAs powders, which can rapidly reduce the κ value. Due to the high hardness of B, ball milling tools can be damaged and easily introduced alloys like Fe, Ni, Co, etc. from the jars and the stainless-steel mill balls. The other major problem is the As vacancies which makes it difficult to obtain perfect lattice. Even after repeating the heat process 4 - 5 times, energy-dispersive X-ray spectroscopy (EDS) results indicate that BAs powder lack of As with a ratio of B:As to be near 3:2. Also, C and Si impurities obtained during the EDS characterization, which is mainly coming from the quartz tube and from the B source.

During this process only, powder BAs phase was obtained and there were no large pieces of crystals. These powders are too small for any local or transport measurement and the only use is, they can be used as a precursor for growing BAs single crystals.

3.2 BAs Synthesis via the Flux Method

Growing single-crystal materials from the flux method are one of the widely used techniques, especially for large-scale crystal growth because of the availability and accessibility. Growth of cubic BAs from the flux method is found to be challenging, since reactions above 920 °C would result in the irreversible formation of $B_{12}As_2$, which limits reaching the melting point of B.²³ Due to the low solubility of B, finding a suitable flux became more difficult.

By looking at the binary phase diagrams (Figure 3.2)⁷² and past research reports,⁷³ Nickel (Ni) is found to be one of the suitable flux for BAs growth. B and Ni are mixed with the ratios of 1:1, 2:3, 3:7 and 1:4, at different temperatures in a sealed quartz ampoule to dissolve B in the liquid phase of Ni to make Ni-B ingot. Once As was added to the mixture, with a temperature below 900 °C, no BAs phase was found in the quartz tube. Cu, Mg, Te, Sb and Zn and their binary mixtures with different ratios have been tried to dissolve B, but none of these worked as a suitable flux. Finally, some binary mixtures like Ni-Bi-B and Ni-Cr-B were also tried but the experimental procedures were limited due to the lack of ternary phase diagrams and no B found to be dissolved in these binary mixtures.

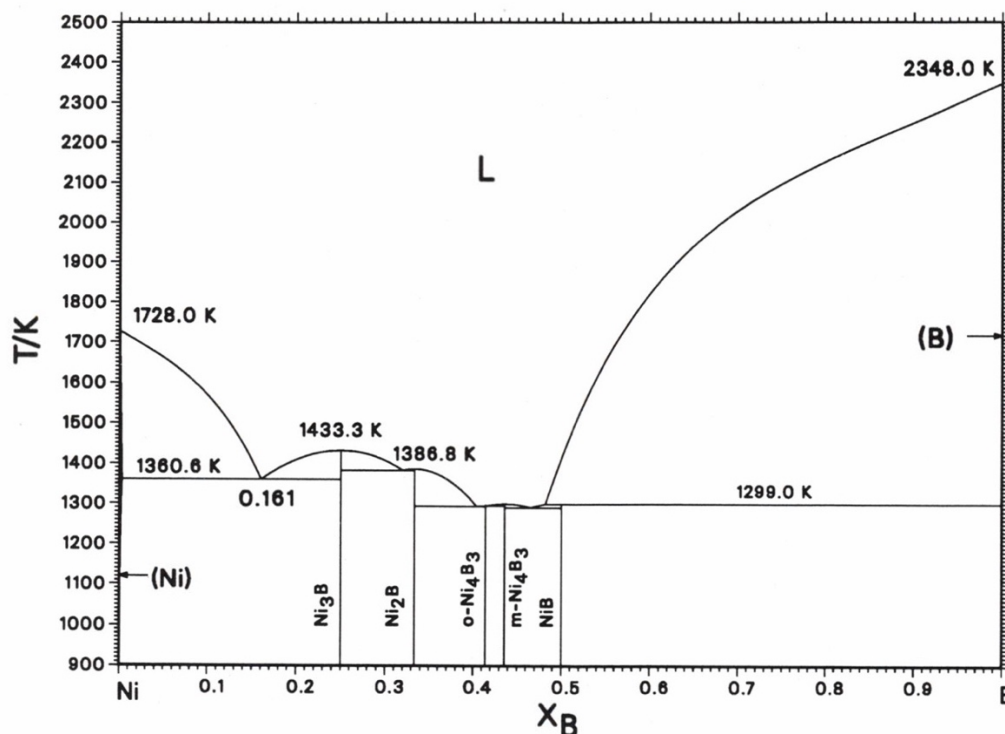


Figure 3.2 Phase diagram of system nickel-boron.⁷²

3.3 BAs Synthesis via Vapor Transport

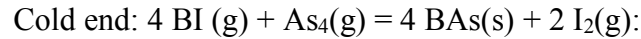
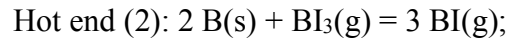
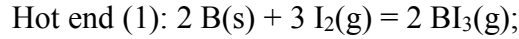
After many failed attempts on flux growth, we started trials to grow cubic BAs single crystals from chemical vapor transport (CVT), which is so far the only successful method to grow BAs.^{2, 3, 67, 71} This method is somehow able to solve the problem of boron's high melting point and was successful in transporting gas-phase boron compounds from source end to growth end using Halogen elements as a transport agent.

3.4 Enhanced CVT Growth

B, As and I_2 are first sealed in a fused quartz tube, where I_2 works as a transporting agent. Then the tube is horizontally placed in a two-zone tube furnace and a temperature gradient is applied. At the hot end, boron reacts with I_2 and form BI_3 vapor, and further reaction makes BI vapor. At the cold end that BI reacts with As vapor and forms BAs and

decomposes back to I_2 vapor. Within the sealed quartz tube, the pressure difference caused by the temperature gradient works as the driving force, which follows the reaction direction determined by the thermodynamic parameters. The sublimation point of As is 615 °C and the melting point is 817 °C which is in the range of the temperatures that we used in the CVT process. Meanwhile, during the crystal growth, both liquid and vapor phases of As were obtained due to the high vapor pressure inside the sealed quartz tube. The density of liquid As is 5.22 g cm⁻³, which is similar to the density of cubic boron arsenide. But we obtained large-high-quality BAs grown inside the liquid As, which indicates the density of BAs is a little bit higher than the calculated values.

In 2006, Dumont and Monteil proposed a thermodynamic calculation that deduces the endothermic behavior of the formation reaction for BAs at temperatures above 1000K;⁷⁴ the reaction is spontaneous at high temperatures, suggesting that the cold-end temperature must be higher than 1000 K.⁷⁵ The higher cold-end temperature (>1073 K) reported for recent impressive progress in high κ of BAs^{4, 76, 77} agrees with such thermodynamic information and shows that this CVT process prefers a hot-to-cold direction. Cueilleron and Viala⁷⁸ reported that, above 500K, the boron triiodide (BI_3) formation reaction is exothermic and experimentally proved the transport of B via BI_3 from the cold end to the hot end. However, the formation of boron monoiodide (BI) is endothermic so that the transport of B via BI is in the hot-to-cold direction. Since hot-to-cold diffusion dominates when the pressure inside the tube is greater than 3 atm,²⁰ which is always true during BAs CVT growth, and considering the fact that flow convection is always from the hot side to the cold side, CVT growth of BAs single crystals prefers the hot-to-cold direction, and the proposed major processes that are more likely to occur are described as follows:



During this process, the amount of I_2 is kept constant, which helps to continuously produce BAs until all the source materials finish. By carefully controlling the growth parameters like amount of source materials, amount of transport agent, temperature gradient and vapor pressure, BAs crystals can grow at the cold end of the quartz tube. During the initial trials, BAs grown at the cold end appear to be bulk crystals with smaller sizes and many defects. Nucleation happens nearly everywhere in the inner wall of the cold end and the maximum size obtained from this was less than $500 \mu\text{m}$. As residues also moved to the cold end of the tube and cover the grown crystals, which prevent direct observation after cooling down the sealed tube to room temperature. Quartz tube opened, carefully picked, cleaned with *aqua regia* [hydrochloric acid (HCl): nitric acid (HNO_3) = 3:1] to completely remove As residues. Based on all these facts further optimizations have taken place to grow large-size high-quality BAs crystals.

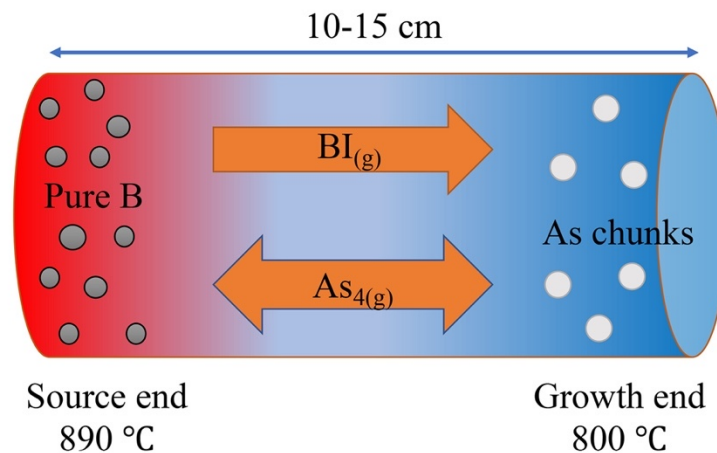


Figure 3.3 Schematic diagram of BAs single crystal growth via horizontal CVT method.

Based on the previous set-ups several experiments have been designed with different temperatures and the results shown in Table 3.1:

Table 3.1 Temperature adjustments of the CVT process.

Hot end temperature T_h (± 5 °C)	Cold end temperature T_c (± 5 °C)	Experimental observations
820	720	Very few bulk crystals with the size less than 0.5 mm
830	730	Very few bulk crystals with the size of 0.5 mm
840	740	Very few bulk crystals with size less than 1 mm
850	750	Few gray bulk crystals with size less than 2 mm
860	760	Few gray bulk crystals with size of 1-2 mm
870	770	Many gray bulk crystals + few red thin crystals with the size less than 1 mm
880	780	Few thin red crystals with the size of 1-2 mm
890	790	Many thin red transparent crystals with the size of 2-3 mm
900	800	Many red transparent crystals with the size of 2-3 mm
910	810	Many large thick gray crystals with the size of 2-3 mm

The growth period is set to two weeks and the amount of source materials and the tube length kept constant for all the experiments. Temperatures between 615 °C and 800 °C were already tried out by other researchers and the results are not that good, these trials only focus on further optimizations to grow better quality BAs crystals. Further optimizations proved that when the hot end temperature is below 820 °C the crystal growth is very limited and in the range of 880 - 900 °C, more boron reacts with iodine to produce large size crystals. Besides, as BAs decompose at 920 °C, the maximum temperature used is 910 °C as the hot end

temperature. Then as the second step, different temperature gradients tried out by keeping constant hit end temperatures at 890 °C and the results are shown in Table 3.2:

Table 3.2 Temperature gradient adjustments to optimize the CVT process.

Temperature gradient ΔT (± 10 °C)	Experimental observations
50	Many gray bulk crystals less than 1 mm in size
60	Many gray bulk crystals less than 1 mm in size
70	Many gray bulk crystals with the size of 1-2 mm
80	Few red crystals up to 1 mm in size
90	Few red crystals with the size of 1-2 mm
100	Many red crystals up to 3 mm in size
110	Many red crystals up to 3 mm in size
120	Many red crystals with the size of 1-2 mm
130	Few red crystals + many gray bulk crystals up to 2 mm
140	Few gray bulk crystals up to 1 mm
150	Few gray bulk crystals up to 1 mm

Note that this CVT process is very sensitive to any minor changes during the growth process. Therefore, all the trials have been repeated to confirm the results. These results only give an overview of the results and sometimes hard to reproduce due to some other phenomena like the purity of source materials, stability of the furnace temperatures, etc. Based on the previous set-ups several experiments have been designed with different length of quartz tubes and the results shown in Table 3.3:

Table 3.3 Tube length adjustments of the CVT process.

Tube length (± 0.5 cm)	Experimental observations
7.0	Many gray color small crystals
8.0	Many gray crystals + few small red crystals
9.0	Many gray crystals + few small red crystals
10.0	Some red transparent crystals + many gray color bulk crystals
11.0	Many large transparent red color crystals
12.0	Many large transparent red color crystals
13.0	Many red color small crystals
14.0	Few bulk gray color crystals
15.0	Very few gray color BAs pieces
16.0	No BAs crystals

Note that, to keep the vapor pressure constant the amount of I_2 and As changed in each tube. From these experiments and combining all these outcomes, we can make some conclusions that at higher hot end temperatures in the range of 880 - 900 °C with a temperature gradient of 80 - 120 °C with shorter tube length (10.0 - 12.0 cm), the BAs crystal growth is preferred.

3.4.1 Seeded CVT Growth

One major challenge during the CVT is the nucleation. Whenever we optimized the other growth parameters, crystals start to grow nearly all over the inner wall of the cold end of the quartz tube. That means, the BAs start to nucleate within a short distance that when the

crystals grow larger, they collide with neighboring crystals and either stop the growth or overlap and make many defects. To avoid this kind of uncontrolled growth, heat treatment, 2% hydrofluoric acid (HF) and clean using alcohols to remove unnecessary stuff tried out, but the progress is very little.

The most effective method is to apply another nucleation site to the growth side of the system.² Applying seeds, actually small BAs crystals obtained from previous growth, work as a starting point and act as a substrate for the nucleation process. Because of the same lattice structure, growing from the seeds are much easier BAs molecules. Based on previous reports^{19, 20} smaller crystals with the size of 10-40 μm are used as seeds. Then the collected seeds were carefully placed in the growth end of the quartz tube, which is very difficult due to the small size of the seeds and easy to stick to the inner wall of the quartz tube. To avoid that issue later tried to use a little bit bigger seeds of 50-100 μm , but it is easy to change the position of the tube during sample preparation because the seed is not permanently attached to any place.

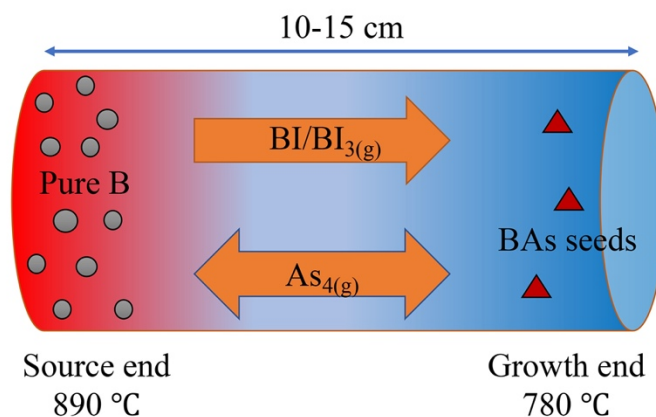
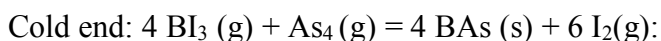
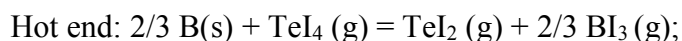


Figure 3.4 Schematic diagram of BAs single crystal growth using seeded CVT method.

Even though, this seeded CVT method increases the amount of crystals grown inside the quartz tube, after cleaning it is difficult to recognize or separate the seeds from the newly grown BAs crystals. Large BAs crystals were obtained using this method but none of these big ones found attached to the seeds.

3.4.2 BAs Growth Using Different Transport Agents

At the beginning of this project, two types of transport agents were used to react with boron and transport the boron compounds to the cold end of the quartz tube. I_2 and tellurium tetraiodide (TeI_4) both worked and BAs crystals obtained from both agents. But due to the slow reaction rate of TeI_4 , the crystals are smaller in size and the amount of crystals obtained from one batch is also small. When the TeI_4 used, the chemical reaction of the CVT growth can be as follows:



The major drawback of using TeI_4 is the excess tellurium (Te) can act as an impurity during the growth period and can combine with the BAs lattice. EDS results confirmed the availability of Te in the crystals grown using TeI_4 . Thermal conductivity of the BAs grown using TeI_4 shows lower values compared to the crystals grown using I_2 .

3.4.3 BAs Growth Using Different Boron Sources

In this part of the project, based on our experimental observations and previous studies by multiple groups,^{4, 76, 77} we focus on one part of the CVT growth mechanism for BAs single crystals: the boron (B) source.²³ Until now, two B sources have been reported for BAs CVT growth: high-purity B and as-grown BAs crystals. Both B sources result in the successful

production of BAs single crystals, but the process details for each vary, especially the reaction rate. By direct comparison of the B sources, we try to gain some insight into the BAs CVT growth, and we believe that our work will guide and support future optimization of the process in order to grow larger-size, higher-quality BAs single crystals.

BAs single crystals were grown by a seeded CVT technique, which was fully described by Tian et al. in 2018.² Different B sources, together with arsenic lumps and iodine powder, were sealed under vacuum and put at the hot end (895 °C) of a fused quartz tube. The other end of the tube served as the growth end and was held at 780 °C. After 2 weeks, millimeter-scale crystals were found, carefully picked, cleaned with *aqua regia*, and ultrasonically bathed to remove contaminants.

For a direct comparison, five different types of B sources were used:

- I. Pure B chunks in the size range of 1–2mm (99.9999%, Alfa Aesar);⁴
- II. As-grown BAs single crystals grown by (I) in the size range of 1–2 mm;
- III. As-grown BAs single crystals grown by (I) in the size range of 0.1–1 mm;
- IV. BAs powder made by hand grinding the as-grown BAs single crystals grown by (I);
- V. As-made BAs precursor made by the direct reaction of B and As inside a quartz tube.⁶⁸

BAs CVT growth using the five types of B sources shown schematically in Figure 3.5.²³ By choosing the BAs crystals with the size and shape similar to B used in Type I growth, we assume that the total surface area of the BAs single crystals in Type II is similar to that in Type I. It should be noted that for Type III, IV and V, the amount of B contained in each BAs source was the same as the amount of pure B used in Type I. Similarly, for Types

III, IV and V, the amount of As used for CVT was reduced by the amount of As contained in each BAs source so that the total amount of As for the CVT was the same in all four reactions. Thus, the total amounts of elemental B and As were the same in Types I, III, IV and V for comparison.

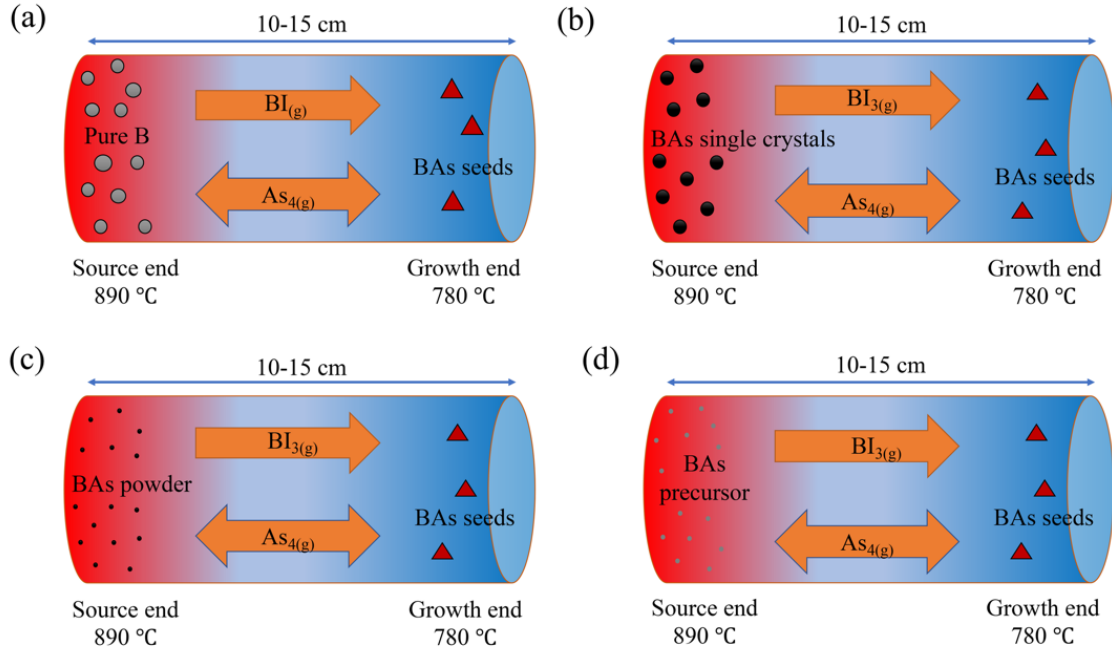
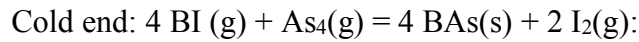
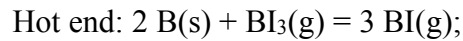
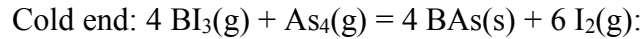
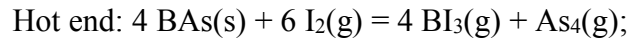


Figure 3.5 Schematic diagrams of CVT growth with different B sources, which is (a) pure B (Type I); (b) as-grown BAs SCs (Type II & III); (c) BAs powder made by grinding the BAs SCs (Type IV); and (d) BAs precursor with high As deficiency (Type V), respectively, located at the hot end and sealed in a fused quartz tube under vacuum.²³

When pure B (Type I) is used as the primary B source:



When as-grown BAs (Types II-V) is used, a different set of reactions occurs:



For the reactions using as-grown BAs single crystals as the B source (Types II-V), it is difficult to conclude whether BI_3 or BI is transporting B atoms to the crystal-growth end, but both products show the endothermic hot-to-cold transfer of BAs. Except for the thermodynamics behind the CVT process, comparisons between Type I and Types II-V clearly prove that the reaction rate of BAs is much faster than that of B. This agrees with the primary observation by Chu and Hyslop in 1972⁶⁷ and Xing *et al.* in 2018.⁷⁰

3.4.4 CVT Growth Using Different Nucleation Sites

BAs crystals normally grow on the inner wall of the quartz tube, where the tube's inner wall is basically a flat surface to the nucleation, so the growth just randomly happens at any point on the cold end. Such uncontrolled nucleation is not preferred if large-sized crystals are desired, but it also suggests that quartz is a good nucleation site for BAs. Hence, we introduced a quartz bar into the tube to serve as the heteronucleation site.⁷⁹ This cylindrical bar with a much larger curvature is very favorable to the nucleation of BAs. We have found that using this technique, nucleation mainly occurred on the bar and large BAs Single crystals were obtained.

We also found that while many of the single crystals grow at various angles to the bar, the largest one grows perpendicular to the bar. Hence, if the bar sits parallel to the tube-length direction, BAs grows within the cross-sectional plane of the tube, and the final size of the single crystal is limited by the tube's diameter; on the other hand, BAs grows along the tube-length direction if the bar is placed perpendicular to the tube-length direction, and the final size of the single crystal is limited by the tube's length. For this experiment, we used 6-mm-diameter quartz tubes, so when the quartz bar was placed parallel to the tube's length direction, the collected crystals were always less than 6 mm in diameter, whereas very long

BAs single crystals were grown on a bar placed perpendicular to tube's length direction as shown in Figure 3.6. Because the tube's length is always much larger than its diameter, placing the quartz bar in a certain position at the growth end will help control the size of the final crystals.

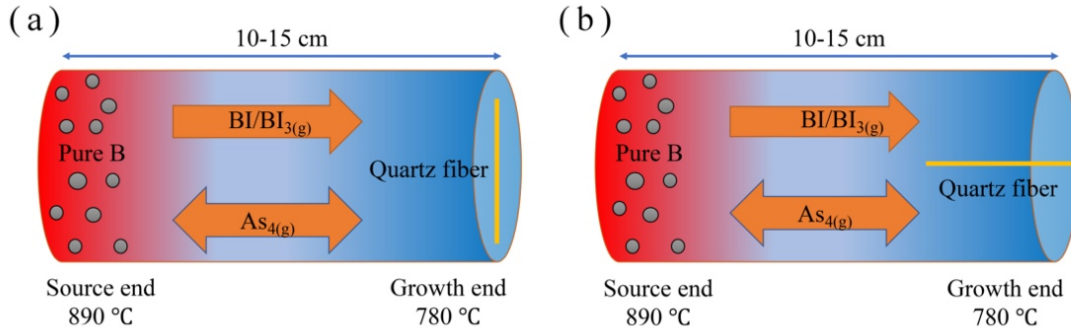


Figure 3.6 Schematic diagrams of CVT growth with different orientations of the quartz fiber bar which is, (a) quartz fiber placed perpendicular to the tube-length direction; (b) quartz fiber placed parallel to the tube-length direction.

To further investigate the influence of the nucleation site on the growth and also thermal conductivity, high-quality gallium arsenide (GaAs) wafers, Si wafers, silicon carbide (SiC), sapphire (Al_2O_3) bars, hexagonal boron nitride crystals (h-BN) and gallium oxide (Ga_2O_3) wafers used as heteronucleation site for BAs single crystal growth. Only GaAs wafers, Si wafers and sapphire found as good nucleation sites to grow BAs, while others did not show any growth of BAs crystals when used as nucleation site in the CVT growth. The problem with the h-BN crystals is similar to BAs seeds because of the smaller size. After clean the samples, it is really difficult to find the h-BN crystals on the growth side of the sealed quartz tube and hard to observe nucleation start on these crystals.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Crystals Grown by CVT Method

Only a few researches reported the successful growth of BAs single crystals. Lv *et al.*'s work on as-grown BAs crystals with multi-domain with the size of 300 - 500 μm and the highest thermal conductivity is around $200 \text{ W m}^{-1} \text{ K}^{-1}$.³ In 2018, Tian *et al.* introduced the seeded CVT growth process and reported the growth of BAs single crystals with the size of 400-600 μm and the thermal conductivity is around $350 \text{ W m}^{-1} \text{ K}^{-1}$.² In this work, we start with following Tian *et al.*'s² work and look into new research pathways to enhance and optimize the BAs growth process to achieve a larger size, high quality and good electrical & thermal properties.

BAs crystals grown from the CVT method mostly started to nucleate in the inner wall of the cold end of the quartz tube. Small crystals in the size of 200 - 600 μm covered the entire cold end of the tube as shown in Figure 4.1(a) & (b). Since they are already attached to each other it was very difficult to do further characterizations. The BAs crystals grown from seeded CVT has two major issues, which are smaller size and irregular morphology. Figure 4.2 shows the optical images of the BAs crystals grown by the seeded CVT method.

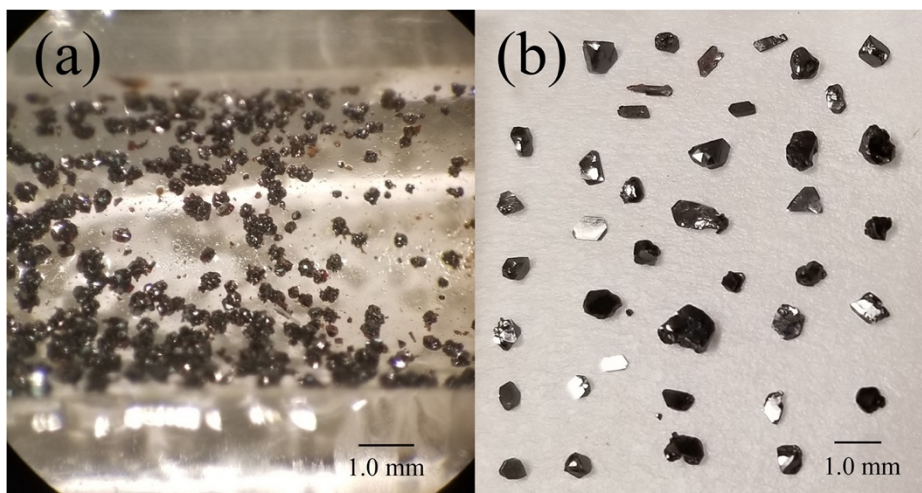


Figure 4.1 Photographs of the representative BAS bulk crystals grown from CVT method. (a) BAS crystal grown on the inner wall of the cold end of quartz tube. (b) Optical image of collected BAS crystals from the quartz tube.

Compared with the traditional CVT process, the seeded CVT gives larger crystals, which indicates higher transport rates of the source materials. But the shape and the surface look irregular, with many grains and cracks visible in the newly grown BAS crystals. Because of these defects, the maximum thermal conductivity achieved from a thin plate-like crystals are around $400 \text{ W m}^{-1} \text{ K}^{-1}$.

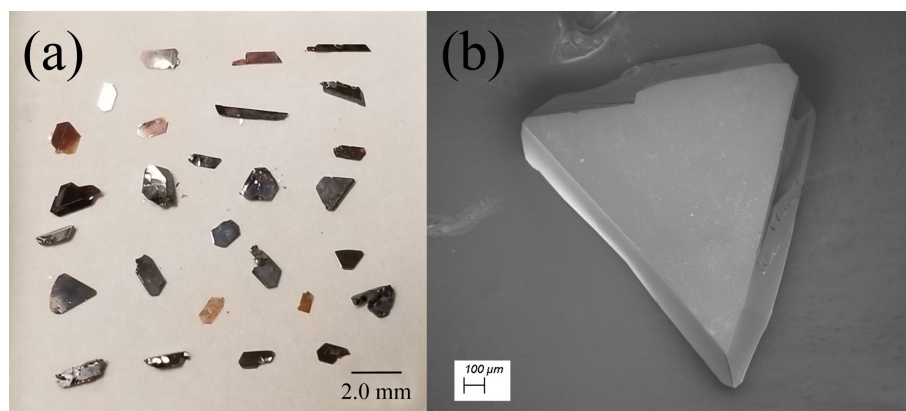


Figure 4.2 (a) Photographs of BAS crystals grown from seeded CVT method. (b) SEM image of BAS crystal grown by seeded CVT after acid washing.

Cleaning the quartz tube to remove all unwanted stuff and etch the inner surface, HF treatments for a couple of hours, ethanol washing and de-ionized water washing all used and

helps to control the nucleation sites. The most effective way found is to introduce large BAs crystals in the size of 0.5 - 1.0 mm as seeds to work as a nucleation site. Figure 4.3 shows the images of the crystals grown by large BAs seeds. Compared to crystals shown in Figure 4.2(b), newly grown crystals have a much cleaner and smoother surface after cleaned using *aqua regia*. After many trials of carefully controlling the growth parameters, thin plate-like BAs single crystal sample obtained and thermal conductivity reached $1100 \text{ W m}^{-1} \text{ K}^{-1}$.⁴

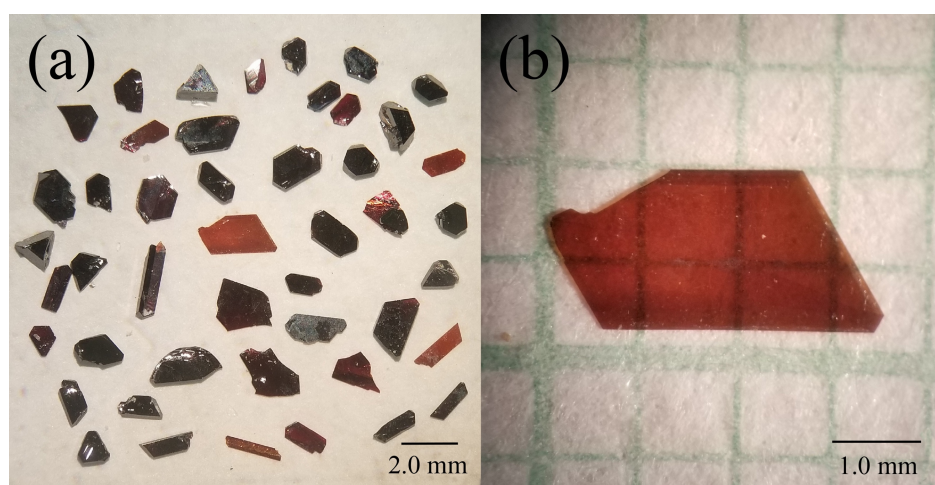


Figure 4.3 (a) Photographs of the BAs single crystals grown from more controlled seeded CVT method. (b) Enlarged image of BAs sample from Figure 4.3(a) which obtained high. Thermal conductivity above $1000 \text{ W m}^{-1} \text{ K}^{-1}$.

Even though the seeded CVT method can grow high-quality BAs crystals, not all the crystals have the same characteristics. As shown in Figure 4.3(a), only a few red-plates like crystals obtained high thermal conductivity. The rest of the crystals from the same grown batch shows lower thermal conductivity due to many surface defects and grains. That is mainly caused by unwanted nucleation and overlapping the newly grown crystals. Seeds somehow help to controlled the nucleation, but still, most of the new growth started in the inner wall of the cold end of the quartz tube. Further investigations were carried out to

optimize the amount of source materials, transport agent and controlling the nucleation to reduce unwanted growth that happens in the inner wall of the quartz tube.

4.2 Effect of Boron Sources on the Growth of BAs

This section is a reprint of my paper (Gamage, G. A.; Sun, H.; Ziyadeh, H.; Tian, F.; Ren, Z., Effect of boron sources on the growth of boron arsenide single crystals by chemical vapor transport. *Applied physics letters* **2019**, *115* (9), 92103).

In this part of the project, we focus on the effect of the CVT growth mechanism from different B sources.²³ Initially different boron sources like magnesium diborane (MgB_2), lithium borohydride (LiBH_4), sodium borohydride (NaBH_4) was used as the B source and no BAs phase was obtained from the CVT method. Due to high pressure from H_2 gas and the toxicity of B_2H_6 , these experiments are extremely dangerous to carry out in an open lab environment. Next, we focused on the BAs growth using precursors and as-grown BAs crystals as the boron source. BAs single crystals were grown by a seeded CVT technique that was fully described by Tian *et al.* in 2018.² Different B sources, together with arsenic lumps (As, Alfa Aesar, > 99.99999+%) and iodine powder (I_2 , Alfa Aesar, 99.999%), were sealed under vacuum (10^{-4} Torr) and put at the hot end (895 °C) of a fused quartz tube. The other end of the tube served as the growth end and was held at 780 °C. After 2 weeks, millimeter-scale crystals were found, carefully picked, cleaned by *aqua regia*, and ultrasonically bathed to remove contaminants.

For a direct comparison, five different types of B sources were used:²³

- I. Pure B chunks in the size range of 1-2 mm (99.9999%, Alfa Aesar);²
- II. As-grown BAs single crystals grown by (I) in the size range of 1-2 mm;
- III. As-grown BAs single crystals grown by (I) in the size range of 0.1-1 mm;

- IV. BAs powder made by hand grinding the as-grown BAs single crystals grown by (I);
- V. As-made BAs precursor made by the direct reaction of B and As inside a quartz tube.⁶⁸

By choosing the BAs crystals with the size and shape similar to the B used in Type I growth, we assume that the total surface area of the BAs single crystals in Type II is similar with that in Type I. It should be noted that for Types III, IV, and V, the amount of B contained in each BAs source was the same as the amount of pure B used in Type I. Similarly, for Types III, IV, and V, the amount of As used for CVT was reduced by the amount of As contained in each BAs source so that the total amount of As for CVT was the same in all four reactions. Thus, the total amount of the elemental B and As were the same in Types I, III, IV, and V for comparison.

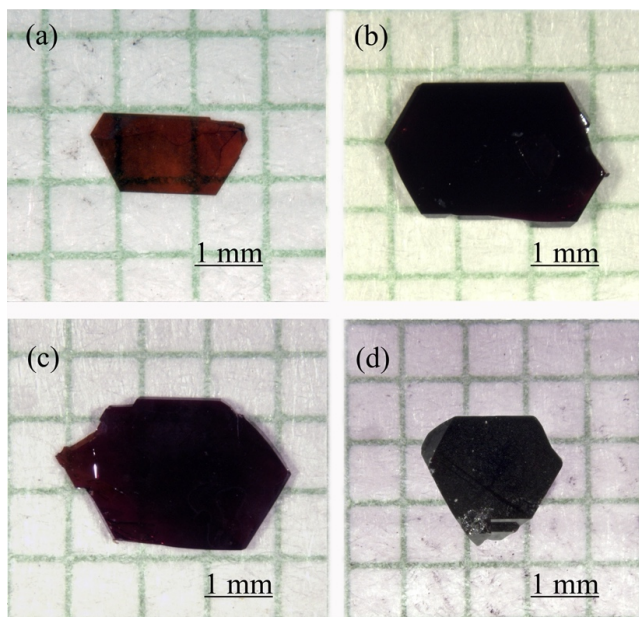


Figure 4.4 Photographs of representative BAs crystals grown from different B sources: (a) small and thin red plate-like crystals from pure B (Type I). (b) Large and thick red crystals from as-grown BAs crystals (Type III). (c) Thin red crystals from BAs powder obtained by grinding the as-grown BAs crystals (Type IV) and (d) small bulk crystals from BAs precursors with As deficiency (Type V), respectively.²³

Crystals grown by different B sources are shown in Figure 4.4 and described in Table 4.1. X-ray diffraction patterns of representative BAs single crystals (Figure 4.5) are presented to show their good quality. The crystals in Figure 4.4(a)-(c) have similar shapes and sizes, but BAs grown using as-grown BAs single crystals or powder as the source produced thicker ($>50\text{ }\mu\text{m}$) plate-like crystals with clean and flat surfaces. Type I pure-B source mostly results in red plate-like crystals less than $50\text{ }\mu\text{m}$ thick. The amount of transported B-source in each reaction (Table 4.1) indicates that as-grown BAs single crystals and powders have faster reaction rates compared to that of the pure B. By using Type V as-made BAs precursor, only a few bulk crystals (Figure 4.4(d)) were formed. They grew on the inner wall of the quartz tube with all dimensions in the range of 1-2 mm. Impurities like Si, C, Fe, Co, Ni are found in the precursors from energy-dispersive x-ray spectroscopy (EDX) analysis, which are probably responsible for the slow transport rate for Type V.

Table 4.1 Statistical description of BAs single crystals grown by different B sources.²³

Type	B source	Percentage of B source transported to the cold end (~%)	BAs crystal sizes (mm)		
			length	width	thickness
I	Pure B, particle size 1-2 mm	25	3 - 5	3 - 5	0.01 - 0.05
II	As-grown BA single crystals in Type I, particle size 1-2 mm	90	1 - 2	1 - 2	0.01 - 0.05
III	As-grown BAs single crystals in Type I, particle size $< 1\text{ mm}$	60	3 - 5	3 - 5	0.05 - 0.1
IV	BAs powder from grinding as-grown BAs single crystals in Type I	30	2 - 3	2 - 3	0.05 - 0.1
V	As-made BAs powder precursor	20	1 - 2	1 - 2	1 - 2

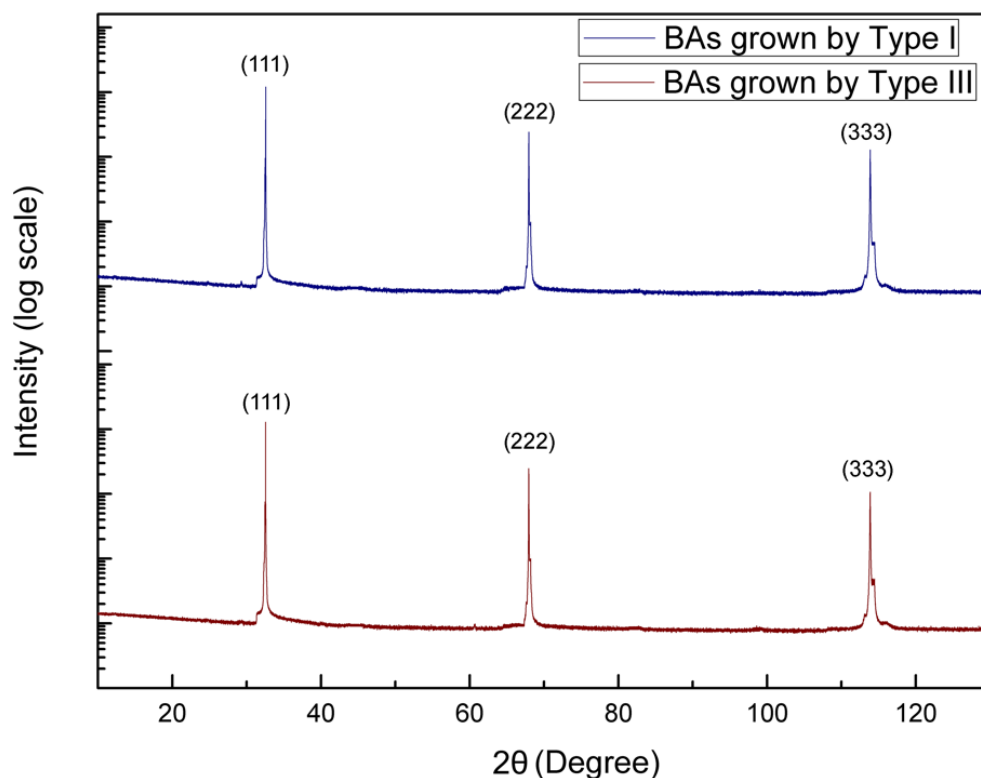


Figure 4.5 Representative x-ray diffraction (Rigaku Smartlab X-Ray Diffractometer, Cu $K\alpha$ radiation source) patterns taken from a carefully selected flat surface of a thin red BAs crystal grown from pure B (Type I) and a thick red BAs single crystal grown from as-grown BAs single crystals (Type III).²³

In addition, Types II, III, and IV proceed with the same crystals but result in single crystals of different sizes and amounts. This indicates that the morphology of the BAs as B sources also leads to different growth rates, *i.e.*, a larger surface area leads to a faster reaction rate and growth rate. The large surface area of the powdered BAs ensures a fast reaction with iodine, but transportation is slower, probably due to unwanted reactions with its impurities, which leads to limited BAs growth at the cold end. The large as-grown BAs single crystals with a smaller surface area slow down the reaction and result in relatively uniform boron transfer. A slower reaction helps to prevent defects forming in the BAs single crystals at the growth end, where the detailed reasons need further studies.

CVT was initially designed as a purification process for excluding impurities from the grown crystals.²⁰ If large-scale production of the precursor crystals can be guaranteed, BAs single crystals grown from the Type II-IV B sources are expected to have fewer impurities leading to higher κ . EDX mapping of an area ($30\ \mu\text{m} \times 20\ \mu\text{m}$) on BAs single crystals from Type I and Type III sources are shown in Table 4.2, along with the atomic percentages of major impurities like Si, C, and O. To avoid the influence of the surface, BAs crystals were broken to expose the interior for characterization of the composition. There is no detectable C in the BAs from Type III and Si impurity is almost 25% less than that from Type I. Impurities of crystals grown from as-grown BAs are fewer than that of those grown from pure B.

Table 4.2 EDX mapping of BAs single crystals from different B sources.²³

Impurities	BAs single crystal from Type I (pure B source) (atomic %)	BAs single crystal from Type III (as-grown BAs source) (atomic %)
C	4.09	0.0
Si	0.92	0.62
O	0.38	0.09
Cu	0.24	0.20
I	0.09	0.08

Lyons *et al.* reported that group iv elements (Si, C, Ge) are strong candidates for causing p-type conductivity in BAs.⁷ Based on their calculations and our experimental observations, to further emphasize the effect of group iv impurities, we performed electrical-transport-property measurements (using the Dynacool Physical Property Measurement System from Quantum Design) on BAs single crystals grown by Type I and Type III sources.

Table 4.3 shows the comparison between electrical resistivity, carrier concentration, and mobility at room temperature on carefully chosen BAs single crystals. The carrier concentration of BAs from Type III is found to be one order of magnitude smaller than that of BAs from Type I. Additionally, the carrier mobility of BAs single crystals from Type III B source is twice as large as that of BAs from Type I B source, which is a clear indication of the low impurity concentrations and As vacancies in the p-type crystals grown using the BAs source.

Table 4.3 Electrical-transport properties of BAs single crystals at RT.²³

Transport measurement	BAs from Type I B source	BAs from Type III B source
Carrier density (cm ⁻³)	2.52 x 10 ¹⁹	1.61 x 10 ¹⁸
Electrical resistivity (Ω cm)	0.00213	0.0115
Mobility (cm ² V ⁻¹ s ⁻¹)	116.3	336.5

Figure 4.6 shows a growing triangular layer within (111) plane over the surface of a red, 3-mm-long, plate-shaped crystal, which is indicating some preferences of the growth process. The nucleation starts from a single point and grows mainly in (111) plane. At the same time, other nucleation may form on the growing layer, leading to secondary growths within the same plane before the growth of the original layer is complete. Defects coming from these secondary growths would finally make the crystals appear in a layered structure with clear boundaries. Similarly, thickness of the grown BAs single crystals increases with increasing growth time. By extending the growth time of Type I, the average thickness of transparent red crystals increased from 0.05 mm (2 weeks) to 0.1 mm (3 weeks) or 0.2 - 0.3

mm (4 weeks). With the same 2 weeks of growth time, crystals grown from an as-grown BAs source (Types II) produced near-opaque and dark red crystals with an average thickness of 0.1 mm, which is consistent with the assumptions of faster reaction rate of the BAs source than the pure B.

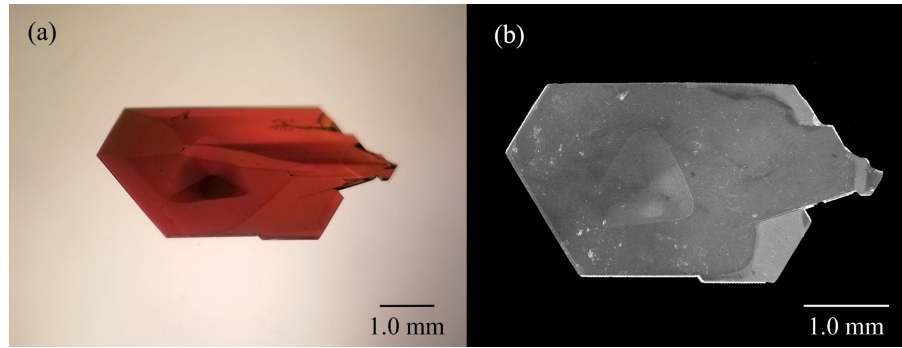


Figure 4.6 (a) Optical and (b) scanning electron microscopy images of a BAs single crystal with new layer growth on the surface.²³

Figure 4.7(a) shows an optical image of a cubic BAs single crystal grown using BAs as B source (Type III) and exhibiting an equilateral triangular shape. This shape is the result of the growth of BAs in the (111) plane as outlined in Figure 4.7(b) for the zinc blende BAs structure. For the growth of cubic structures like Si, the (111) facet has the closest atoms, along which is the fastest and the most reproducible direction.⁸⁰

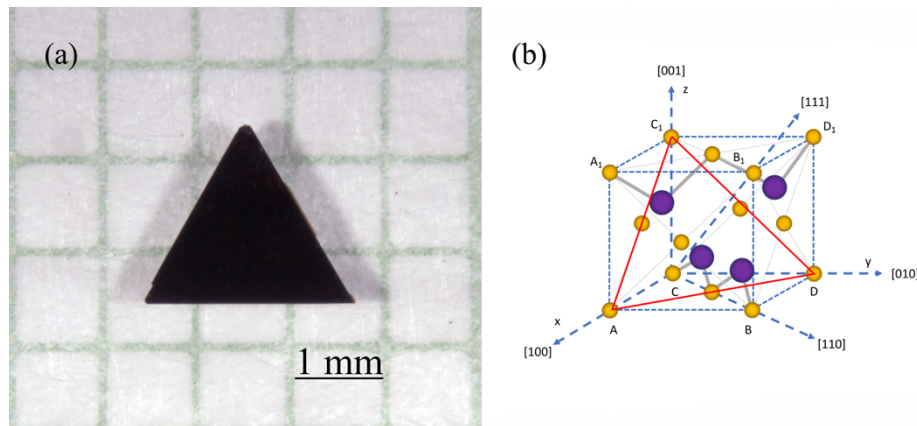


Figure 4.7 (a) Optical image of a triangular crystal. (b) Lattice structure of zinc blende BAs.²³

As has been mentioned by different groups,^{7, 8} impurities or dopants in the grown BAs single crystals have a huge effect on their properties, especially their thermal conductivity and band gap. However, even by B sources of 99.9% purity and later 99.9999% purity, it is difficult to completely avoid Si from raw B.^{7, 76} Hence, purification of the B source is a key to achieve good BAs single crystals. An additional experiment with only B or B₂O₃ powders sealed in a quartz tube with the hot-end temperature of 890 °C was performed. After 2 weeks, additional white powder, later proven by EDX to be SiO₂, appeared in the quartz tube. This observation indicates that both B and B₂O₃ react with the quartz tube, introduce Si-B compounds into the reactions, and finally dope Si into the grown BAs crystals. In addition, some SiO₂ residue is also found in the voids inside the BAs crystals. Thus, Si originates not only from the initial B,⁷ but also from the quartz (SiO₂) serving as the reaction kettle for CVT. This is a major origin of the Si impurity in the grown BAs crystals. Other containers need to be used to avoid possible elemental diffusion from the container to the products.

To summarize, growth of BAs single crystals using different B sources was studied and the experimental comparison clearly shows that using high-quality as-grown BAs as the B source results in faster growth with less impurities. Additionally, if the purity of the raw B can be further improved, BAs single crystals grown by CVT would surely achieve higher thermal conductivity in the future. One last important point is that the observation of the preferred growth direction along the (111) facet of BAs enables nucleation and direction control for the growth. These finds are quite possible to jointly contribute to a more elaborate CVT process and finally result in an industrial-welcome BAs film growth on some selected substrates.

4.3 Crystals Grown by Different Transport Agents

In this part of the project, we focus on the effect of the CVT growth mechanism from different transport agents. BAs single crystals were grown by the CVT technique with quartz fiber as nucleation sites (Further discussed in Section 4.4). B powders (99.9999%, Alfa Aesar), together with arsenic lumps (As, Alfa Aesar, > 99.99999+%) and different transport agents, were sealed under vacuum (10^{-4} Torr) and put at the hot end (895 °C) of a fused quartz tube. The other end of the tube served as the growth end and was held at 780 °C. After 2 weeks, millimeter-scale crystals were found, carefully picked, cleaned by *aqua regia*, and ultrasonically bathed to remove contaminants.

For a direct comparison, two different types of transport agents were used:

- I. Iodine powder in the size range of 1 - 2 mm (99.999%, Alfa Aesar);
- II. Tellurium tetraiodide (TeI_4).

Crystals grown by two of these transport agents are shown in Figure 4.8 and described in Table 4.4. The crystals in Figure 4.8(a) have a much cleaner surface and transparent, but BAs grown using TeI_4 produced much thicker with rough surface (Figure 4.8(b)). Some spots in the BAs crystals in Figure 4.8(b) can be seen in red color, which indicates the nonuniformity of the thickness of the crystals. Since the amount of source materials and the amount of I_2 is the same for Type I and II, indicates that Type II has slower reaction rates compared to Type I.

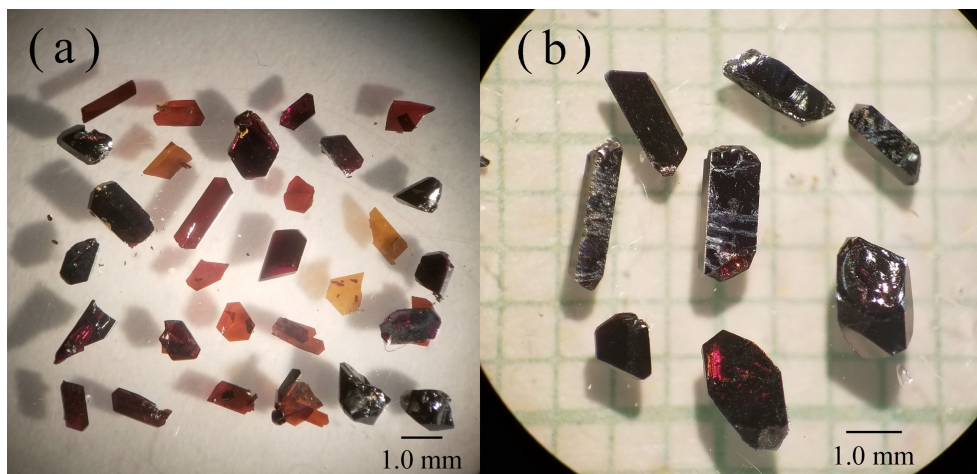


Figure 4.8 Photographs of BAS crystals grown from CVT process with (a) I_2 as the transport agent. (b) TeI_4 as the transport agent.

XRD patterns of representative BAS single crystals from both transport agents show the (111) facet, confirming both have the same crystalline nature. But tellurium (Te) was found in the surface as well as the cross-sections of Type II crystals from EDX analysis, which indicates that somehow Te atoms go into the crystal structure as an impurity. The thermal conductivity of those samples was measured using an optical pump-probe technique called time-domain thermoreflectance (TDTR) and listed the values in Table 4.4.

Table 4.4 Statistical description of BAS single crystals grown by different transport agents.

Type	Transport agent	Surface morphology	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)
I	I_2 powder	Thin reddish color plates-like BAS crystals with smooth surface	1020 ± 110
II	TeI_4 powder	Mostly thick reddish or gray color BAS crystals with rough surface	430 ± 80

4.4 Crystals Grown by Different Nucleation Sites

This section is a reprint of my paper (Gamage, G. A.; Chen, K.; Chen, G.; Tian, F.; Ren, Z., Effect of nucleation sites on the growth and quality of single-crystal boron arsenide. *Materials Today Physics* **2019**, *11*, 100160).

Same CVT growth process was used in this part of the project.^{2, 23} High purity boron (B, United Mineral & Chemical, 99.9999%), arsenic (As, Alfa Aesar, >99.99999%), and iodine (I₂, Alfa Aesar, 99.999%) are placed at the source end (890 °C) of a quartz tube, a piece of quartz bar is placed at the growth end (780 °C), and the tube is sealed under vacuum (10⁻⁴ Torr). As has been reported by many groups, BAs crystals normally grow on the inner wall of the quartz tube. The tube's inner wall is basically a flat surface to the nucleation, so the growth just randomly happens at any point on the inner wall. Such uncontrolled nucleation is not preferred if large-sized crystals are desired, but it also suggests that quartz is a good nucleation site for BAs. Hence, we introduced a quartz bar into the tube to serve as the heteronucleation site. This cylindrical bar with a much larger curvature is very favorable to nucleation of BAs. We have found that using this technique, nucleation mainly occurred on the bar and a 7 mm long BAs single crystal (Figure 4.9(a), (c)) was obtained, the X-ray diffraction pattern for which is shown in Figure 4.9(d). We also found that while many of the single crystals grow at various angles to the bar, the largest one grows perpendicular to the bar (Figure 4.9(b)). Hence, if the bar sits parallel to the tube-length direction, BAs grows within the cross-sectional plane of the tube, and the final size of the single crystal is limited by the tube's diameter; on the other hand, BAs grows along the tube-length direction if the bar is placed perpendicular to the tube-length direction, and the final size of the single crystal is limited by the tube's length. For this experiment, we used 6 mm diameter quartz tubes, so

when the quartz bar was placed parallel to the tube's length direction, the collected crystals were always less than 6 mm in diameter, whereas the 7 mm long BAs single crystal (Figure 4.9(a)) was grown on a bar placed perpendicular to tube's length direction. Because the tube's length is always much larger than its diameter, placing the quartz bar in a certain position at the growth end will help control the final crystals size.⁷⁹

We used the time domain thermoreflectance (TDTR) method to characterize the κ of this 7 mm long sample at room temperature, similar to previous reports.^{4, 76, 77} An 80 nm thick aluminum transducer layer was deposited onto the BAs sample surface by an e-beam evaporator. A laser pulse train with 800 nm central wavelength and 80 MHz repetition rate was generated from a Ti:sapphire laser oscillator. A beam splitter was used to divide the beam into pump and probe beams. The intensity of the pump laser was modulated sinusoidally by an electro-optic modulator (EOM) at 3 MHz, focused on the metal surface with a 30 μm diameter ($1/e^2$) and 45 mW power, and acted as a heating source that generated a temperature change at the metal surface. The probe laser pulse was delayed by a motorized translation stage, focused and overlapped with the pump spot at the metal surface with a 10 μm diameter ($1/e^2$) and 10 mW power. Thermoreflectance of the probe beam as a function of the delay time was recorded by a Si photodiode, the output of which was connected to a lock-in amplifier (LIA) working at the EOM frequency. The phase (PHI) of the LIA as a function of the delay time, which is determined by thermal transport in the material system, was taken as the measured signal. A three-dimensional Fourier heat conduction model for the Al-BAs structure was built to fit the measured data and to extract the κ of the BAs substrate along with the interface thermal conductance between the metal layer and the BAs sample. As shown in Figure 4.10(a), the fitting curve agrees well with the measured phase signal, yielding

a RT κ of $960 \pm 90 \text{ W m}^{-1} \text{ K}^{-1}$, quite close to the reported values when no heteronucleation sites are introduced.^{4, 76, 77} The simulated curves using κ 20% larger or smaller than the fitted one are well separated away from the measured signal, showing the excellent sensitivity of the measurement. As shown in Figure 4.10(b), the uncertainty of the fitted κ was estimated by the standard deviation of the Gaussian distribution of a simulation of 600 TDTR measurements using the Monte Carlo method,⁸¹ which considers both the experimental noise and the propagation of the error of the known parameters in the model.

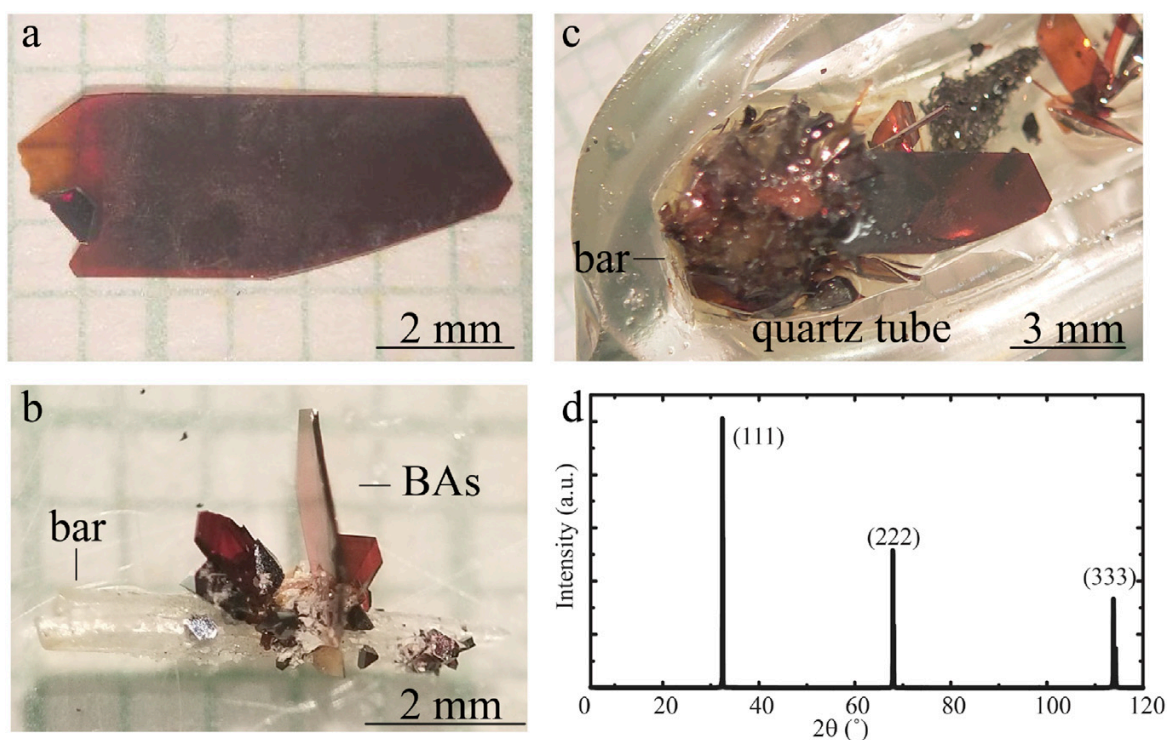


Figure 4.9 Photographs of (a) the obtained 7 mm long BAs single crystal and (b) growth of BAs single crystals on a quartz bar. (c) Photograph of the 7 mm long BAs single crystal sitting inside the quartz tube after acid washing. The quartz bar located at the bottom of the tube (left end) where most of the growth happened. There was growth from the tube wall at other positions as well. (d) X-ray diffraction (Cu $K\alpha$ source) pattern of the 7 mm long BAs single crystal shown in (a), whose sharp (111), (222), and (333) peaks indicate that it is truly single crystal.⁷⁹

To further investigate the influence of the nucleation site on the growth and also thermal conductivity, high-quality GaAs, Si, and sapphire (Al_2O_3) bars were each chosen to serve as the heteronucleation site for BAs single crystal growth. After the same 2 weeks growth time, several-mm-long BAs single crystals were collected from the GaAs bar, whereas on the Si and sapphire bars, only some small pieces of BAs single crystal were found. The maximum room temperature κ values obtained from the BAs single crystals grown from different nucleation sites are shown in Figure 4.11. The room temperature κ values of BAs single crystals grown on quartz ($1240 \pm 100 \text{ W m}^{-1} \text{ K}^{-1}$) and GaAs ($1240 \pm 110 \text{ W m}^{-1} \text{ K}^{-1}$) bars are close to the predicted value, whereas the maximum κ values of the BAs crystals grown on sapphire and Si bars are much lower.

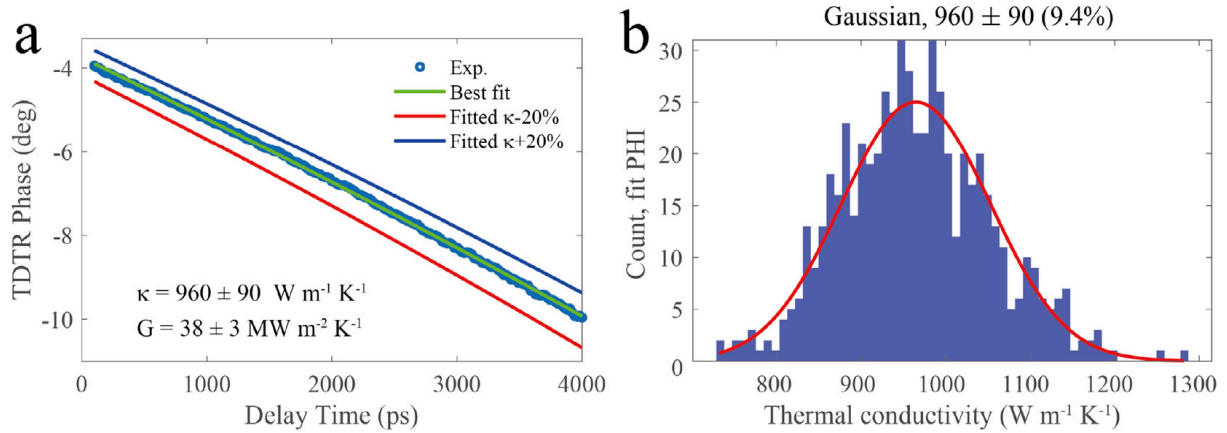


Figure 4.10 (a) TDTR phase signal of the BAs sample, along with its best fitting curve and simulated curves using thermal conductivities 20% larger and smaller than the fitted value. (b) Distribution of the fitted thermal conductivities from a Monte Carlo simulation of 600 TDTR measurements.^{79, 81}

Because the κ (especially ultrahigh κ) value is highly sensitive to various defects, the κ data clearly show the effects of different nucleation sites and on the quality of each grown BAs SC. In the previously reported BAs single crystal growth techniques in which high κ values were obtained,^{4, 76, 77} the growth environment initially includes four compositions: B, As, I_2 , and quartz. It should be noted that a small amount of Si impurity coming from the

quartz tube,²³ as well as commonly occurring defects (i.e., twin boundaries,⁴ vacancies,³ and antisite pair⁸²), are understood to be responsible for the failure to grow uniform BAs single crystals. In this case, when a quartz bar is selected as the heteronucleation site, there are no other kinds of material introduced, and the quality of the final product will not be affected, which can be proven by the observed near record high κ value. In addition, GaAs is quite stable in this environment below 900 °C, so a GaAs bar works as well as a quartz bar as the nucleation site. However, when sapphire is used as the nucleation site in a quartz tube, it reacts with halogens (I_2),^{83, 84} which disturbs the reactions in the CVT process and suppresses the high κ . A similar situation occurs when Si is used ($Si + 2 I_2 = SiI_4$).⁸⁴ Hence, both quartz and GaAs nucleation sites lead to high quality BAs single crystals, whereas Si and sapphire nucleation sites result in low κ .

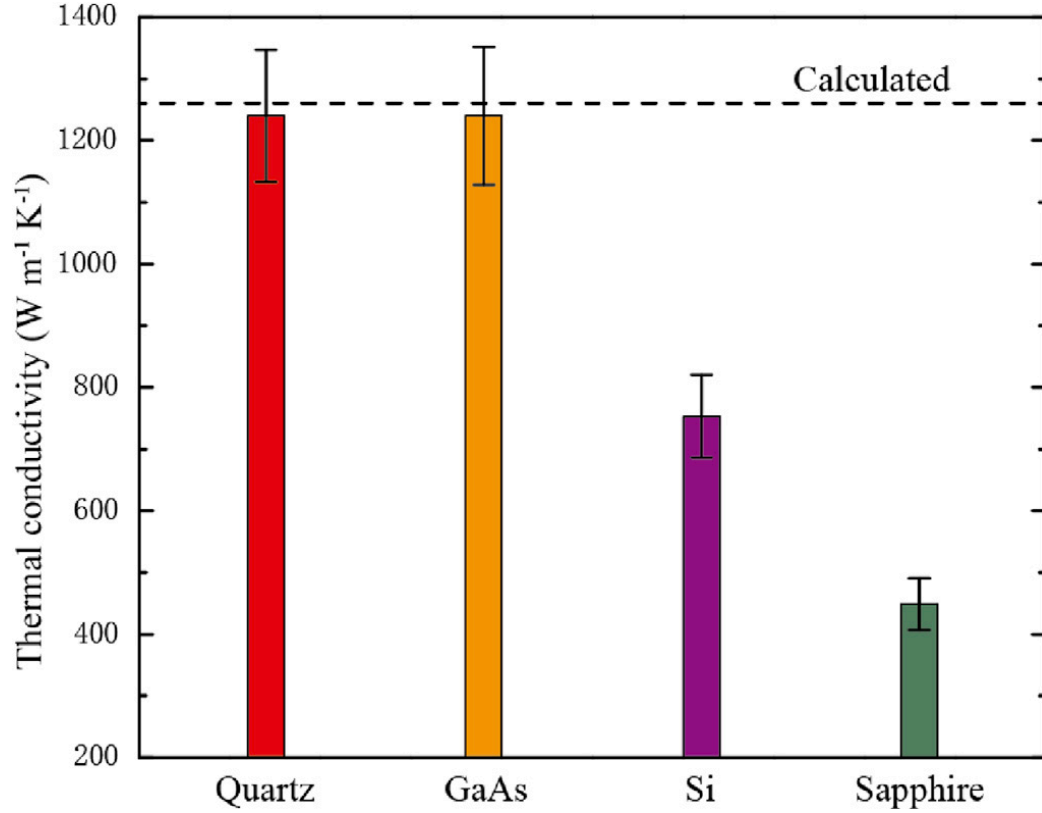


Figure 4.11 Maximum room temperature κ data measured by the same TDTR method (details described in Figure 4.10) from BAs single crystals grown using different nucleation sites. Uncertainty for the κ values was estimated by using the Monte Carlo method.⁸¹ The dashed line represents the calculated room temperature κ for BAs considering 3-phonon, 4-phonon, and phonon-isotope scattering.⁴ Three representative samples for each case of different nucleation sites are measured.⁷⁹

To summarize, we have grown a 7 mm long BAs single crystal by a nucleation site introduced CVT method. A quartz or GaAs bar, serving as heteronucleation site, is placed at the growth end and helps control the nucleation position and growth direction. By confirming the near record high room temperature κ value of the obtained crystal by TDTR, we conclude that the introduction of the quartz or GaAs bar provide some control on the nucleation sites of BAs and does not reduce the intrinsic ultrahigh κ . We believe our findings will provide insight into determining how to grow larger and better BAs single crystals and will help establish the foundation for studying and designing BAs-based devices.

4.4.1 From Quartz Fiber

To further investigate the use of nucleation sites, different sizes of quartz fibers were used in the CVT growth process and every time different sizes of BAs crystals were obtained. When used a long fiber with a thinner diameter, many of the BAs crystals grown perpendicular to the bar (Figure 4.12). By using short fiber pieces, we obtained BAs single crystals that start the nucleation at one single point of the sharp edges of the fiber.

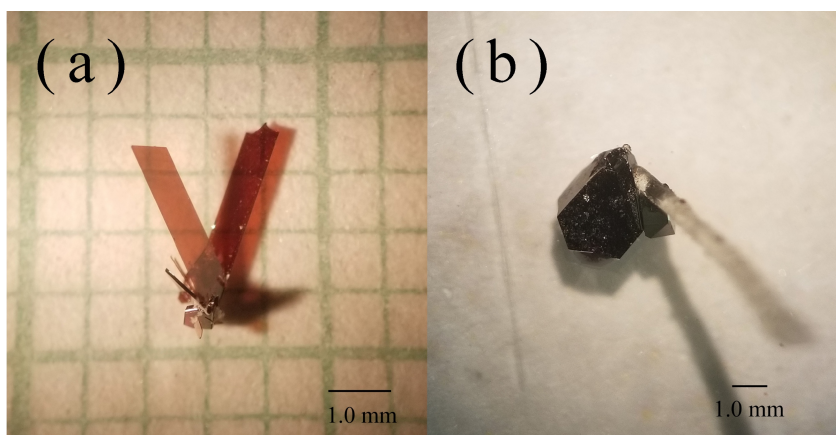


Figure 4.12 (a) BAs crystals grown using quartz fiber as nucleation site. Fiber is perpendicular to the plane. (b) BAs crystal nucleate on quartz fiber and grown perpendicular direction to the fiber.

Newly grown large BAs single crystals using quartz pieces (2 - 4 mm in length) with sharp edges are shown in Figure 4.13. These pieces can be removed from the fiber and used for further characterizations. To keep the small fiber pieces at the right position, the tube was heated after placing the fiber and that way pieces get melted and attached to the tube.

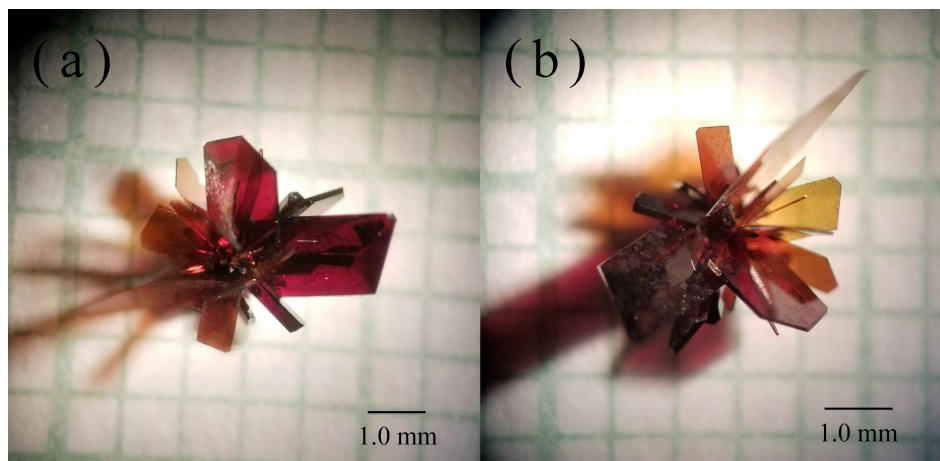


Figure 4.13 High-quality BaS crystals grown using quartz fiber pieces with sharp edges. These crystals started to nucleate at the sharp edges of the fiber.

4.4.2 From GaAs Wafer Pieces

The second type of nucleation site that successfully grows BaS is the GaAs wafers. GaAs wafer cuts into bar shape pieces and is placed in the growth end of the quartz tube. After 2 weeks growth period growth end of the quartz tube was opened and cleaned using *aqua regia*. Most of the BaS crystals grown using GaAs wafer bars are very thin, transparent and red in color. Figure 4.14 shows the two sets of batches grown using GaAs bars as nucleation sites.

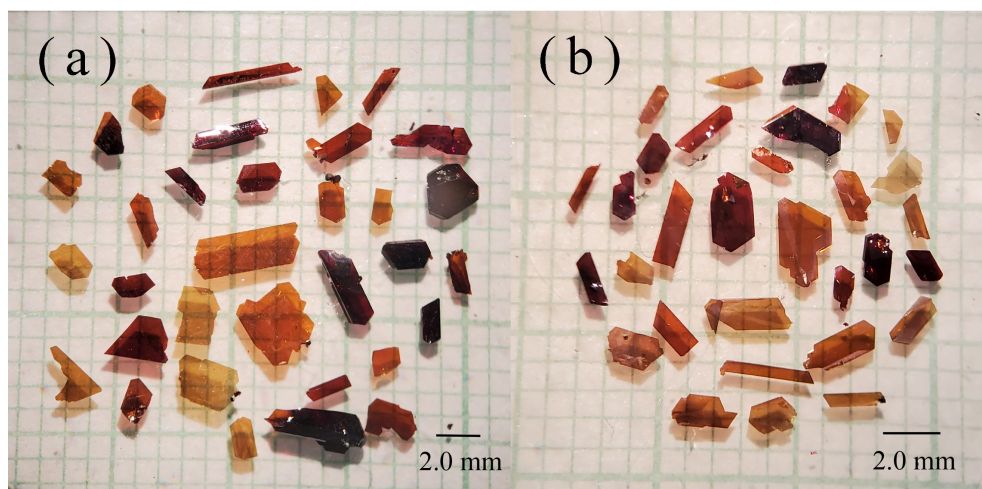


Figure 4.14 High-quality BaS crystals grown using GaAs wafer bars as nucleation sites.

4.4.3 From Si, SiC and Sapphire

Morphology of the newly grown BAs using Si and sapphire as nucleation sites were different from the previous BAs samples. As shown in Figure 4.15, most of the BAs show a thin needle shape with red in color. Si and Aluminum (Al) were found in the surface of BAs crystals from EDX analysis, which indicates that these nucleation sites are the source of impurities. It is key to limit the nucleation numbers to get larger crystals, however, the hetero materials are a source of contamination to affect the κ value. The thermal conductivity of those samples was measured using TDTR and room temperature values are always less than $750 \text{ W m}^{-1} \text{ K}^{-1}$ and $450 \text{ W m}^{-1} \text{ K}^{-1}$ for Si and sapphire respectively. No BAs single crystals were found when using SiC as the nucleation sites. After acid washing, SiC bars came out with no BAs attached.

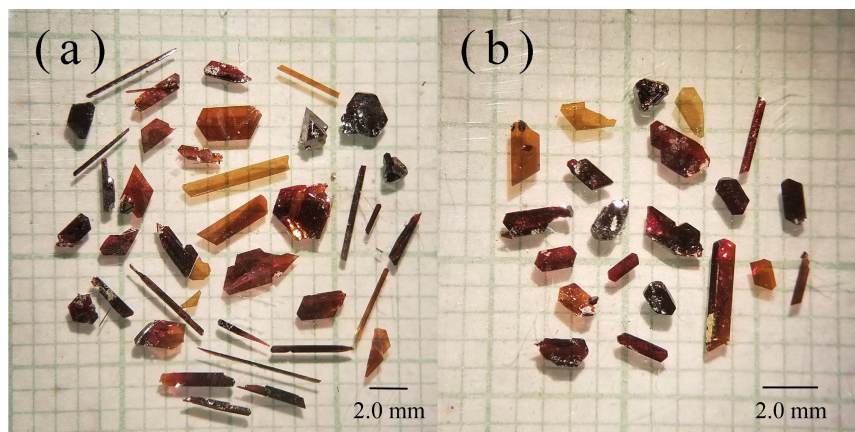


Figure 4.15 Good quality BAs crystals grown by (a) Si as the nucleation sites. (b) Sapphire as the nucleation sites.

4.4.4 Other Nucleation Sites

Recently, h-BN crystals and Ga_2O_3 wafers were tried out as nucleation sites. The problem with h-BN is the smaller size (0.1 – 1.0 mm) and no BAs crystals were found attached to the crystals after 2 weeks of growth. With Ga_2O_3 , we cut the wafer into 1 mm x 1

mm x 3 mm bar shape pieces and placed them in the growth end of the tube. After 2 weeks growth period, a lot of small gray color BAs crystals were found in the Ga₂O₃ bar, but none of these crystals are large enough for measurements. The maximum size of BAs crystals achieved was around 1.5 mm.

4.5 Characterization Results

Electrical transport measurements were carried out on carefully picked BAs samples. After cleaned using *aqua regia*, BAs crystals were washed using acetone and ultrasonic bath to remove excess organic impurities. Electrical resistivity, Hall measurement, heat capacity and magnetic measurements were carried out using Quantum Design PPMS.

4.5.1 Electrical transport Measurements

Temperature-dependent Hall and resistivity measurements were carried out on carefully picked and cleaned BAs single crystals. Most of the BAs samples show an increase in resistivity with the increase in temperature from 10 – 300 K, which is metallic behavior. The average room temperature hole carrier concentration of our BAs lies in the range of 10^{17} – 10^{19} cm⁻³ (Figure 4.16). Most of the metallic samples have low carrier mobility. But some of the high-quality BAs samples with semiconducting nature (electrical resistivity drops with increasing temperature) show high bulk mobility and the highest bulk mobility obtained from BAs single crystals grown using GaAs nucleation sites is around 650 cm² V⁻¹ s⁻¹.

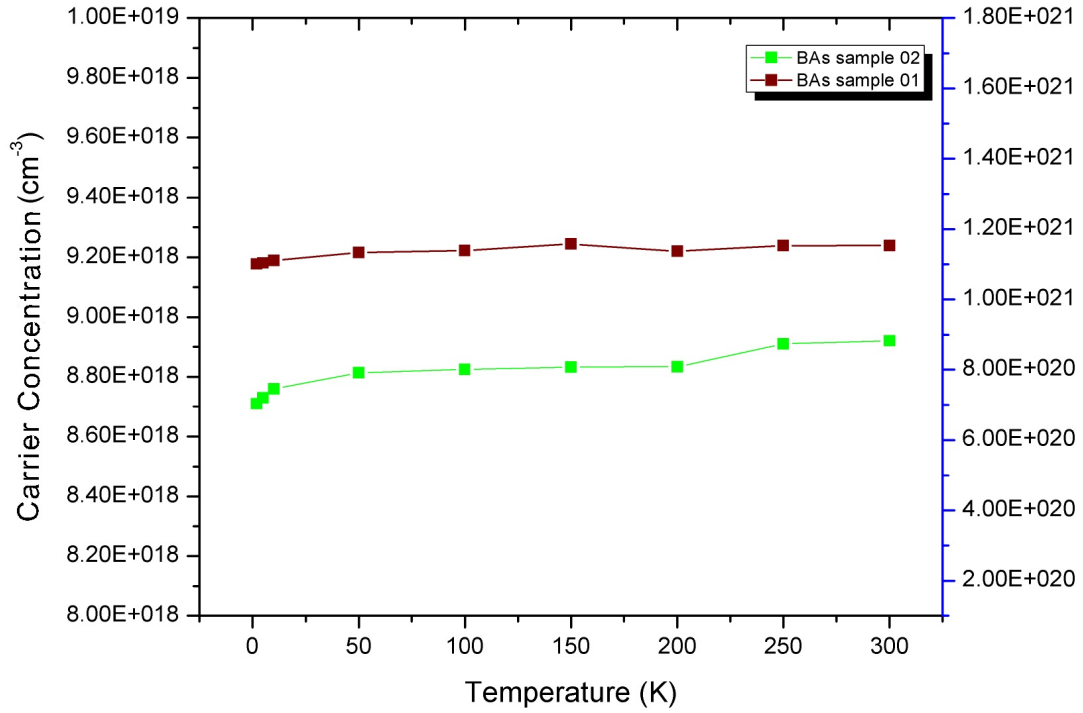


Figure 4.16 Temperature dependent Hall measurement results. Carrier concentration of two BAs samples grown using quartz fiber (Sample #01) & GaAs wafer (Sample #02) as nucleation sites.

Some of the BAs samples grown using quartz fiber or GaAs wafer bars as nucleation sites showed the semiconductor behavior as shown in Figure 4.17. Even though bulk mobility of such samples shows a maximum of $650 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, local optical measurements performed in the same samples show local carrier mobilities up to $1500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at selected spots. But even in the same BAs crystal, different spots measured by optical measurements show different carrier mobility values and different thermal conductivities, which proves the nonuniformity and the defects in the as-grown BAs crystals.

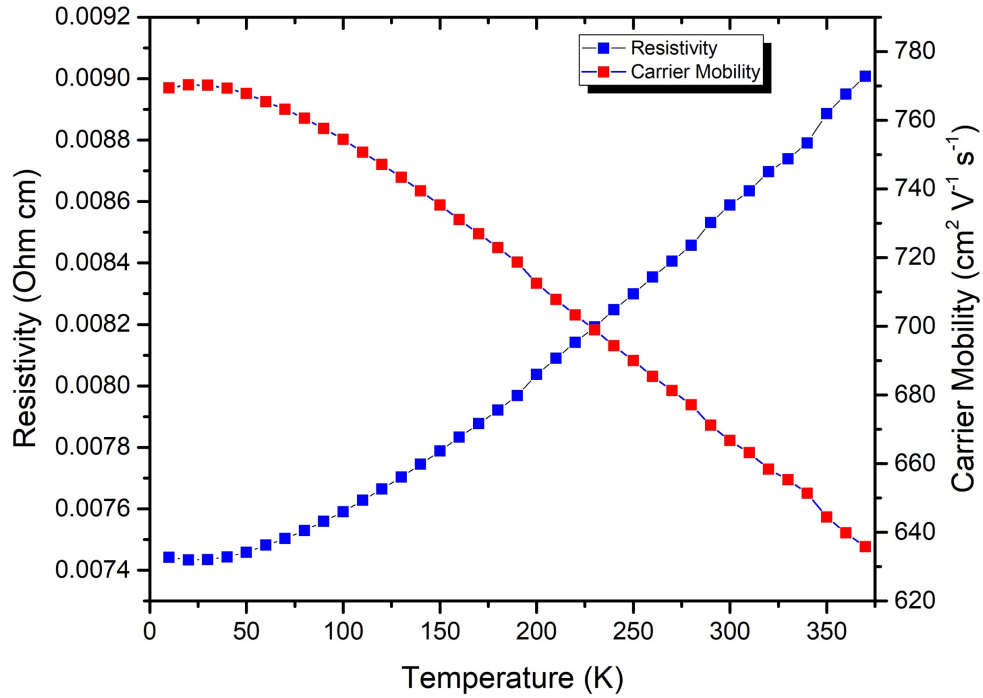


Figure 4.17 Temperature dependent electrical resistivity and carrier mobility data.

4.5.2 Thermal Measurements

We discovered ultrahigh but non-uniformly distributed thermal conductivity (κ) in BAs single crystals using TDTR technique with micrometer resolutions. In this method, 80 nm thick aluminum layer was deposited onto the BAs sample by a e-beam evaporator. BAs crystal heats up using a high-power 58 μm diameter pulsed pump laser and monitored the subsequent heating/cooling process with a low-power 9 μm diameter probe pulse delayed by a motorized translation stage. Thermoreflectance as a function of delay time was recorded by a Si photodiode, which was connected to a lock-in amplifier (LIA). A three-dimensional Fourier heat conduction model for Al-BAs structure was built to fit the measured data and extracted the κ value. We used the same TDTR platform to measure the κ of a synthetic diamond crystal. The measured values are in good agreement with theoretical calculations.

We found a sharp decrease in κ as temperature increases. The figure shows 4.18 shows the temperature-dependent κ measurements from Tian *et al.*'s⁴ paper comparing the measured values with the theoretical calculations. This was the first time we obtained highest κ of BAs for one single spot in a sample with the value of $1160 \pm 130 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature.⁴ The other data shown in the Figure 4.18 are as follows: calculated κ versus temperature for BAs (black) and diamond (green) including only three-phonon scattering (dashed lines) and both three- and four-phonon scattering (solid lines). Measured κ for diamond by TDTR (green diamonds). Measured κ for BAs Sample #1 (solid red symbols) and #2 (open red symbols) by TDTR, Sample #3 by Frequency domain thermoreflectance (FDTR - solid orange star for mean value), steady-state (open blue squares) and lock-in Raman (open brown square) methods, and Sample #5 by the steady-state method (solid blue squares). Also shown are the fits to measured steady-state and TDTR κ for BAs (blue and red solid lines, respectively), and reported measured κ for GaN⁴⁰ and GaAs⁸⁵ (magenta and purple triangles, respectively). The error bars for the TDTR and FDTR data represent one standard deviation and were obtained via Monte Carlo simulations and derivative matrix-based analysis of uncertainty propagation, respectively. The error bars for the steady state and lock-in Raman measurement results were calculated by propagating random errors at 95% confidence and systematic errors.

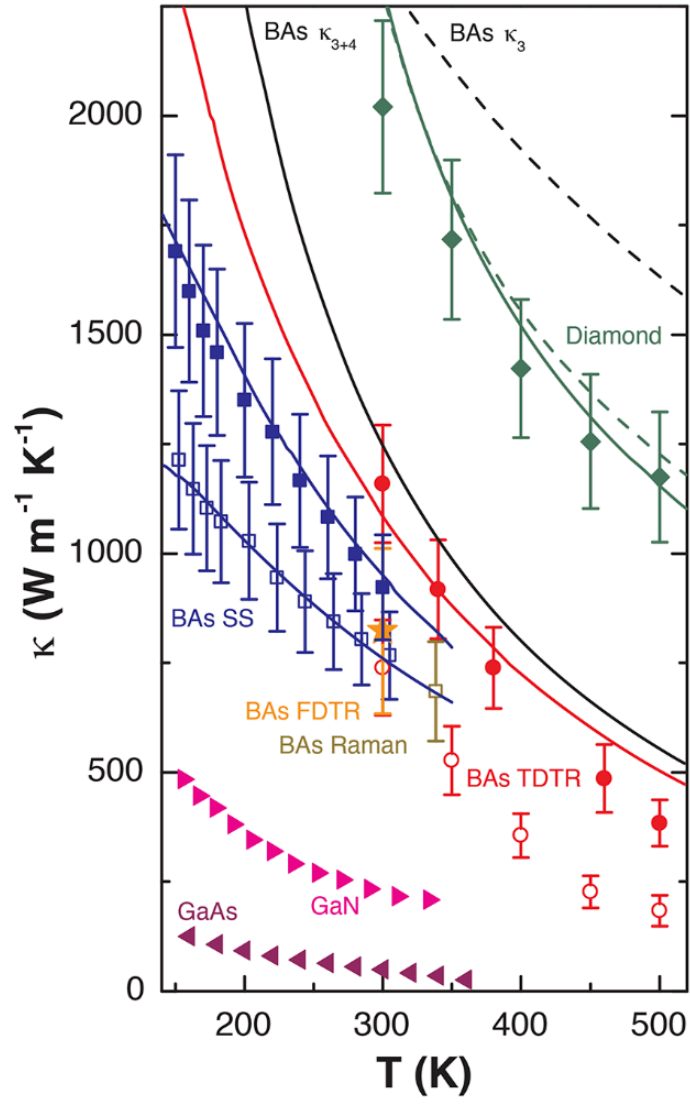


Figure 4.18 Measured thermal conductivity of BAS in comparison with theoretical calculations and other crystals.⁴

Room temperature carrier concentration, resistivity, bulk carrier mobility and thermal conductivity of BAS samples grown using different nucleation sites are shown in Table 4.5.

Table 4.5 Room temperature carrier concentration, resistivity, carrier mobility and thermal conductivity data for BAs samples grown using different nucleation sites.

Nucleation site	Carrier Concentration (cm^{-3})	Resistivity ($\Omega \text{ cm}$)	Bulk mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Local mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)
GaAs wafer bar	5.40×10^{17}	0.017	670	1610	1240
Quartz fiber	1.60×10^{18}	0.006	640	1500	1240
Quartz pieces	2.40×10^{18}	0.0045	585	1000	1150
Si wafer bar	1.89×10^{19}	0.0023	157	410	753
Sapphire bar	1.28×10^{20}	0.001	48	135	449

4.5.3 Optical Measurements

This section is a reprint of my paper (Yue, S.*; Gamage, G. A.*; Mohebinia, M.; Mayerich, D.; Talari, V.; Deng, Y.; Tian, F.; Dai, S. Y.; Sun, H.; Hadjiev, V. G.; Zhang, W.; Feng, G.; Hu, J.; Liu, D.; Wang, Z.; Ren, Z.; Bao, J., Photoluminescence mapping and time-domain thermo-photoluminescence for rapid imaging and measurement of thermal conductivity of boron arsenide. *Materials Today Physics* **2020**, *13*, 100194).

Even though BAs being first studied in the late 50s of the last century,⁶⁸ its actual bandgap value has not been well settled. The bandgap from the latest first-principles DFT calculations by several independent groups begins to merge but still falls in a wide range from 1.7 to 2.1 eV.^{6-8, 86} The bandgaps from earlier calculations were too low (1.0 eV - 0.3 eV).^{87, 88}

Experimentally, earlier studies put the bandgap down to 1.4 - 1.5 eV;⁸⁹⁻⁹¹ latest low-temperature photoluminescence (PL) combined with hybrid functional calculations brought the bandgap up to 1.78 eV.⁷

In this work, we first experimentally determine the BAs bandgap using optical absorption spectroscopy and then report the observation of room temperature band-edge PL. The bandgap is the most important property of a semiconductor, it is also an essential parameter for theoretical calculation and forms the basis for optical, electronic, as well as thermal properties.⁹² To experimentally obtain BAs bandgap, we grew thin single crystals using a recently reported method and chose optical absorption spectroscopy to directly measure its bandgap.^{23, 64, 75} Figure 4.19(a) shows UV-Visible absorption spectra of three representative samples at room temperature in Tauc plot as an indirect semiconductor. The nature of indirect bandgap semiconductors is quickly confirmed because, despite their differences in absorption at lower energy tails, all of them exhibit the same and well-defined absorption edge. The intersections give us a bandgap of 1.82 eV, which falls in the range of the latest DFT calculations.^{6-8, 86}

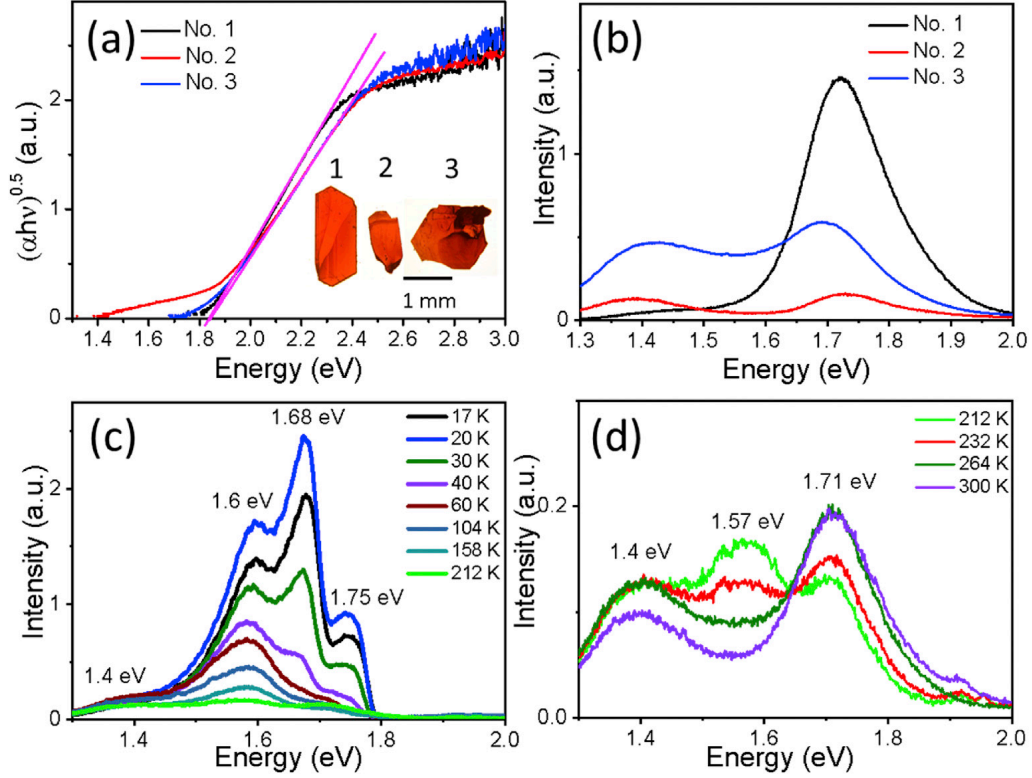


Figure 4.19 Optical absorption and photoluminescence spectra of BA crystals. (a) Indirect bandgap Tauc plots of UV-Visible absorption spectra of three BA crystals. Inset: optical transmission images. (b) Room temperature PL spectra of the samples. (c-d) Evolution of PL of a BA crystal as a function of temperature (c) from 17 to 212 K and (d) from 212 to 300 K.⁶⁵

Compared to UV-Vis, PL is more sensitive to the crystal quality, defects, and doping levels.⁹² Because the recent high κ demonstrations are actually successful stories of material synthesis of high-quality BA crystals, we performed PL spectroscopy at room temperature although earlier BA samples exhibited no PL at all.³ Despite being an indirect semiconductor, the samples reported here show very strong PL as displayed in Figure 4.19(b), indicating a much better crystal quality. The spectra feature a high energy peak at 1.72 eV and a relatively weak peak at 1.4 eV. A close comparison between the PL and absorption spectra reveals a close relationship: Sample #1 with a weak absorption below the absorption edge exhibits a dominant PL peak at 1.72 eV, while Samples #2 and #3 with stronger absorption at the absorption tails also exhibit a strong PL at the same energy. We conclude that the 1.72 eV

peak is the band-edge-associated PL. The 1.40 eV peak comes from sub bandgap defect states, which is believed to be responsible for the observed bandgap values in earlier reports.⁸⁹⁻⁹¹

The room temperature PL in Figure 4.19(b) has less spectral features than that of recently observed PL at 10 K which was claimed to be dominated by defect-bound excitons, donor-acceptor transitions, and free exciton transition observed only under a strong excitation.⁷ To complete the PL spectra comparison, we varied the temperature and monitored the evolution of PL. As can be seen from Figure 4.19(c) and (d), the PL at 17 K resembles the reported features very well in a study by Lyons *et al.*⁷ and confirms the peak at 1.72 eV as owing to band-edge free exciton transitions. As temperature increases, the intensity of all three major peaks decreases and begins to merge. At ~160 K, the bound exciton peak is merged into the free exciton peak. At ~260 K, the donor-acceptor transition peak disappears. The disappearance of these peaks at higher temperatures is due to thermal excitation of loosely bound electrons and holes. In contrast, the intensity of the defect state at 1.40 eV changes very little, proving that it is from a different origin.

4.5.4 Photoluminescence Mapping & TDTP Results

This section is a reprint of my paper (Yue, S.*; Gamage, G. A.*; Mohebinia, M.; Mayerich, D.; Talari, V.; Deng, Y.; Tian, F.; Dai, S. Y.; Sun, H.; Hadjiev, V. G.; Zhang, W.; Feng, G.; Hu, J.; Liu, D.; Wang, Z.; Ren, Z.; Bao, J., Photoluminescence mapping and time-domain thermo-photoluminescence for rapid imaging and measurement of thermal conductivity of boron arsenide. *Materials Today Physics* **2020**, *13*, 100194).

In addition to the uncertainty in its basic bandgap, current κ measurement methods are difficult to meet the demand for rapid screening of κ for development of BAs for future device applications. X-ray diffraction and transmission electron microscopy were used to prove the high crystal quality of BAs in recent demonstrations,^{4, 76, 77} but it is well known that these techniques are not very sensitive to impurities, point defects, and doping levels, which are important for phonon dynamics and transport.^{1, 34} Time-domain thermoreflectance (TDTR) was used by all three groups to determine κ of BAs,^{4, 76, 77} but it is a very specialized technique that requires expensive lasers, sophisticated data collection, analysis and interpretation.^{57, 81, 93, 94} TDTR also requires a complicated sample preparation step: the surface of the sample must be polished to be flat enough and is then coated with a metal film that serves as both a laser absorber and a thermal transducer.^{57, 81, 93, 94} Other methods, such as one-dimensional heat transport method coupled with Raman temperature sensing, require even more careful sample preparation, so they are not widely used.⁴ It should be noted that κ is much harder and more challenging to measure than temperature, especially for high κ materials because it involves rapid local material heating and temperature sensing.

Based on well-established relationship between PL and crystal quality and the relationship between crystal quality and thermal conductivity κ proved by recent demonstrations and theories, we speculate that a strong PL must lead to a high κ . To make use of these relationships for thermal conductivity measurement, we take one step further and utilize confocal PL imaging to evaluate κ of large BAs crystals. Figure 4.20 shows the optical pictures and PL mappings of three BAs crystals at room temperature. The PL mapping was performed with a custom confocal laser-scanning fluorescent microscope using a 532 nm 40 mW pulsed diode laser to raster scan the sample surface and a GaAsP photomultiplier tube

(PMT) with sensitivity in the range of 300 - 720 nm. A 635 nm long pass filter was used to block PL excitation. Depending on the mapping size and resolution, PL mappings of millimeter sized samples takes seconds or less to complete, and a real time PL mapping is also easy to achieve. Despite apparent single crystal sample, PL mappings reveal a nonuniform intensity (Figure 4.20(b) and (d)) across the smooth surfaces (Figure 4.20(a) and (c)), which indicates a nonuniformity of crystal quality in the same crystalline surface. PL mapping further reveals very different domain patterns (Figure 4.20(f) and (h)) on the opposite surfaces of the same BAs crystal (Figure 4.20(e) and (g)). The measured κ values shown in Figure 4.20(d) will be explained in details in the next paragraph.

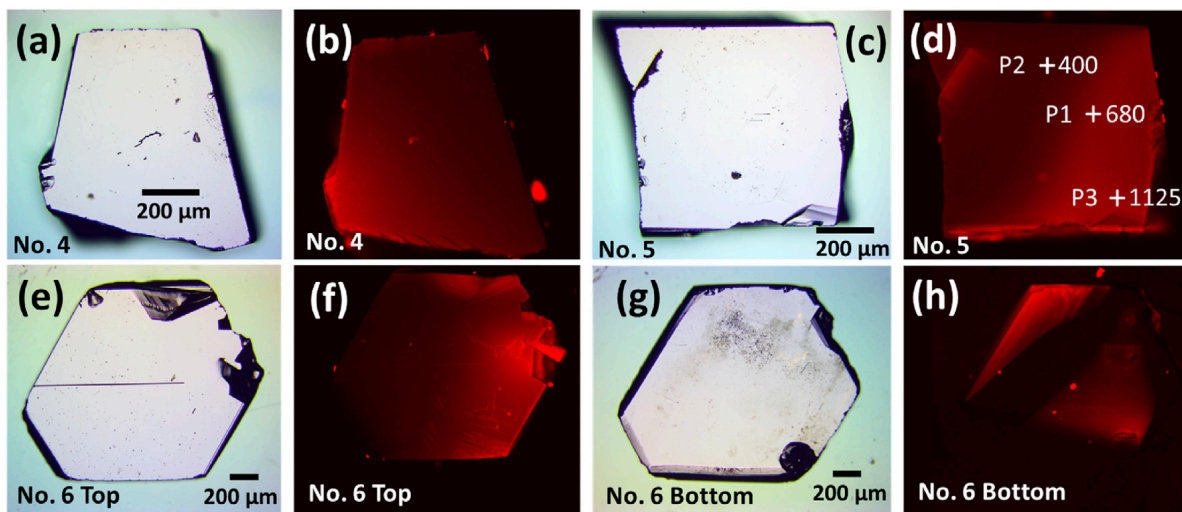


Figure 4.20 PL mapping of three BAs samples. Optical images (a, c) and PL mappings (b, d) of samples No. 4 and No. 5. The selected spots P1-3 are marked by “+” along with their κ measured with TDTP. Optical images (e, g) and PL mappings (f, h) of opposite surfaces of sample No. 6.⁶⁵

Temperature affects the PL spectrum of a material in many ways; conversely, the spectral changes can be used to measure a sample's temperature. Figure 4.21(a) shows an example of temperature PL shift. The spot P1 was chosen from sample No. 5 as shown in Figure 4.20(c) and (d). The spectrum from spot P1 is shown in Figure 4.21(a). As the

temperature increases, the PL peak intensity remains the same, but the short wavelength spectral region becomes enhanced (Figure 4.21(a)). We believe this is due to increased rate of optical transitions of thermally excited electrons and holes that involve absorption of phonons around the indirect bandgap. To use this temperature dependent PL spectrum as a sensitive temperature marker in TDTP, we use a band-pass optical filter to select a short wavelength band and then use a fast PMT to measure the integrated intensity over that band. The spectrum of that band is shown in Figure 4.21(a) and (b) shows an almost linear dependence of the integrated PL intensity as a function of temperature; this same curve will be used to determine the sample temperature.

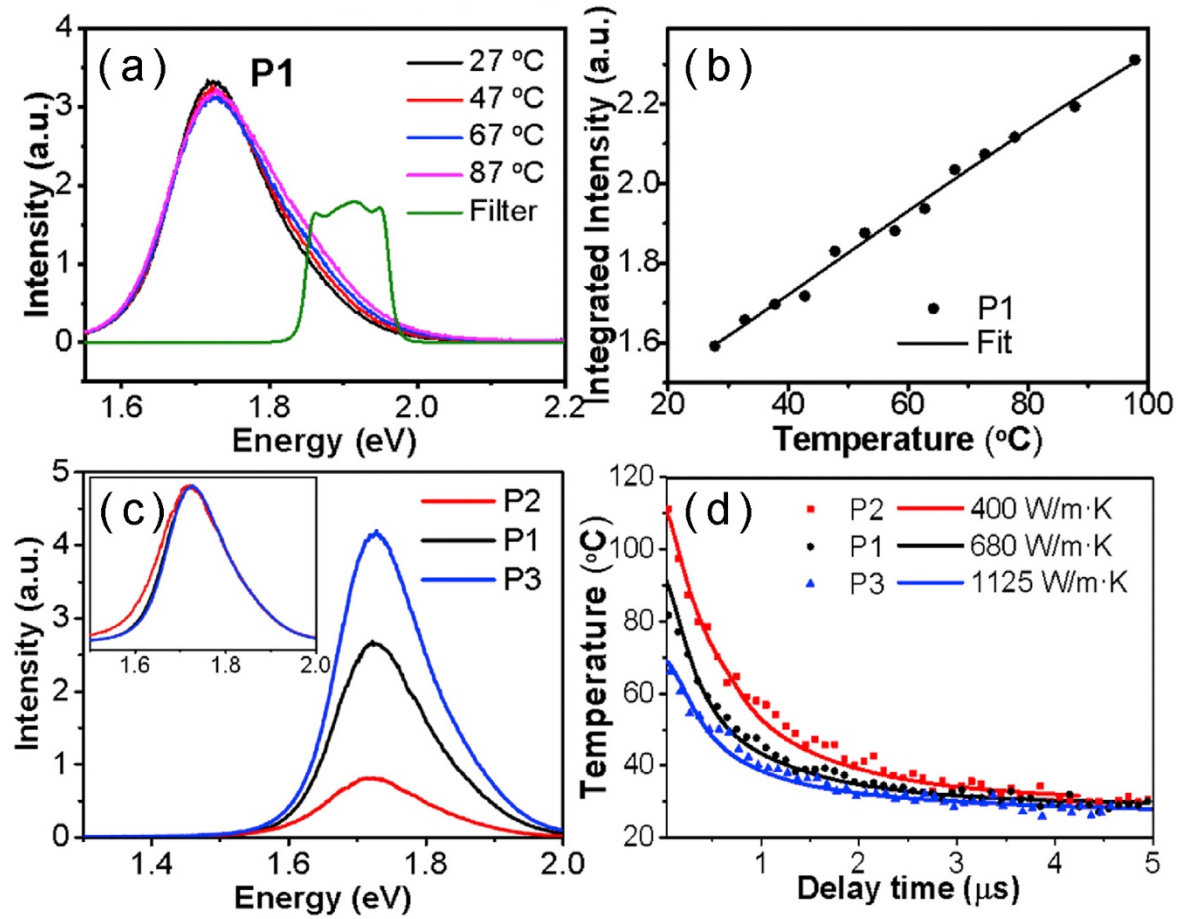


Figure 4.21 Time-domain thermo-photoluminescence (TDTP). (a) Temperature-dependent photoluminescence spectrum of the spot P1 in Figure 4.20(c) and (d), and the transmission spectrum of a filter used to select the spectral window for TDTP. (b) PL intensity integrated over the transmission window as a function of temperature. (c) Photoluminescence spectra of spots P1, P2 and P3 as shown in Figure 4.20(c) and (d). (d) TDTP traces for P1, P2 and P3, and simulated curves.⁶⁵

To make a good comparison and estimate for the whole sample, we chose two more spots P2 and P3 from the PL mapping in Figure 4.20(c) and (d). Figure 4.21(c) shows their PL spectra; note that the spot with stronger PL also has a narrower PL line width. Figure 4.21(d) shows their TDTP temperature evolutions. It is very clear that the spots P1 and P3 have lower average temperatures, indicating higher κ values. The temperature differences among the three spots are the greatest right after the excitation of pump pulse owing to their different κ values, and both the temperatures and their differences drop quickly in a few μs owing to fast

heat diffusion. Using any commercial heat transport software, we can fit TDTP curves with k as a parameter. The simulation results with SIMULIA ABAQUS or COMSOL (These are commercial software) shown in Figure 4.21(d) give us a room temperature κ of $680 \text{ W m}^{-1} \text{ K}^{-1}$ for the stronger PL spot P1 and $400 \text{ W m}^{-1} \text{ K}^{-1}$ for the weaker PL spot P2 (their spot locations are shown in Figure 4.20(d)). The highest κ corresponding to the strongest PL spot P3 in Figure 4.20(d) reaches $1125 \text{ W m}^{-1} \text{ K}^{-1}$, in agreement with the recent demonstrations by TDTR.^{4, 76, 77} It should be noted that although recent four-phonon scattering theory has reduced the predicted thermal conductivity from 2200 to $1400 \text{ W m}^{-1} \text{ K}^{-1}$, its calculations are very computationally expensive and are difficult to be verified through experiment or other methods.⁴⁴ In addition, the theory has never accounted realistically for phonon-defect scattering in BAs and that its most accurately predicted κ values are for crystals that still show the signature of defects.

Having shown the power of PL mapping and TDTP, we note that some region of the sample No. 6 in Figure 4.20(g) and (h) exhibited weak or no PL even though it was grown by the same recently reported method.⁷⁵ In fact, our early BAs samples before this work also exhibited no PL.³ Because TDTP is not applicable to samples without PL, we developed another technique that requires little sample preparation as PL mapping and TDTP to quickly prove that samples with no PL have a much lower κ . Figure 4.22(a) shows the experimental setup. Here a continuous wave (CW) laser is used to induce local heating, and an infrared thermal camera is used to monitor the temperature evolution directly. To have a good comparison, we chose three samples with similar sizes and thickness. Figure 4.22(b) shows their optical images, and their PL spectra are shown in Figure 4.22(c); Sample No. 7 was from our early batch that does not show PL.³ The other two were recently grown,⁷⁵ but sample No. 9

has a much stronger PL than No. 8. Figure 4.22(d) shows that, for all three samples, the temperature at the laser focus point increases quickly initially and eventually reaches a plateau. Simulation with COMSOL gives us thermal conductivity κ of $160 \text{ W m}^{-1} \text{ K}^{-1}$ for sample No. 7. Figure 4.22(e) shows snapshots of surface temperatures for the three samples at 40 ms; a much high temperature and large temperature gradient at the laser spot on the sample No. 7 is seen, further confirming that the sample with no PL has lower κ owing to poor crystal quality. However, the technique fails to distinguish samples No. 8 and No. 9, both of them reached similar temperatures despite their huge difference in PL intensity. Apparently, this failure is due to the slow mechanical switching of the CW laser, slow millisecond response of the thermal camera, and the simplified boundary conditions that make realistic simulation difficult. Nevertheless, the infrared thermal images in Figure 4.22(e) have allowed us to identify a sample with low thermal conductivity and given us a vivid picture of heat transfer.

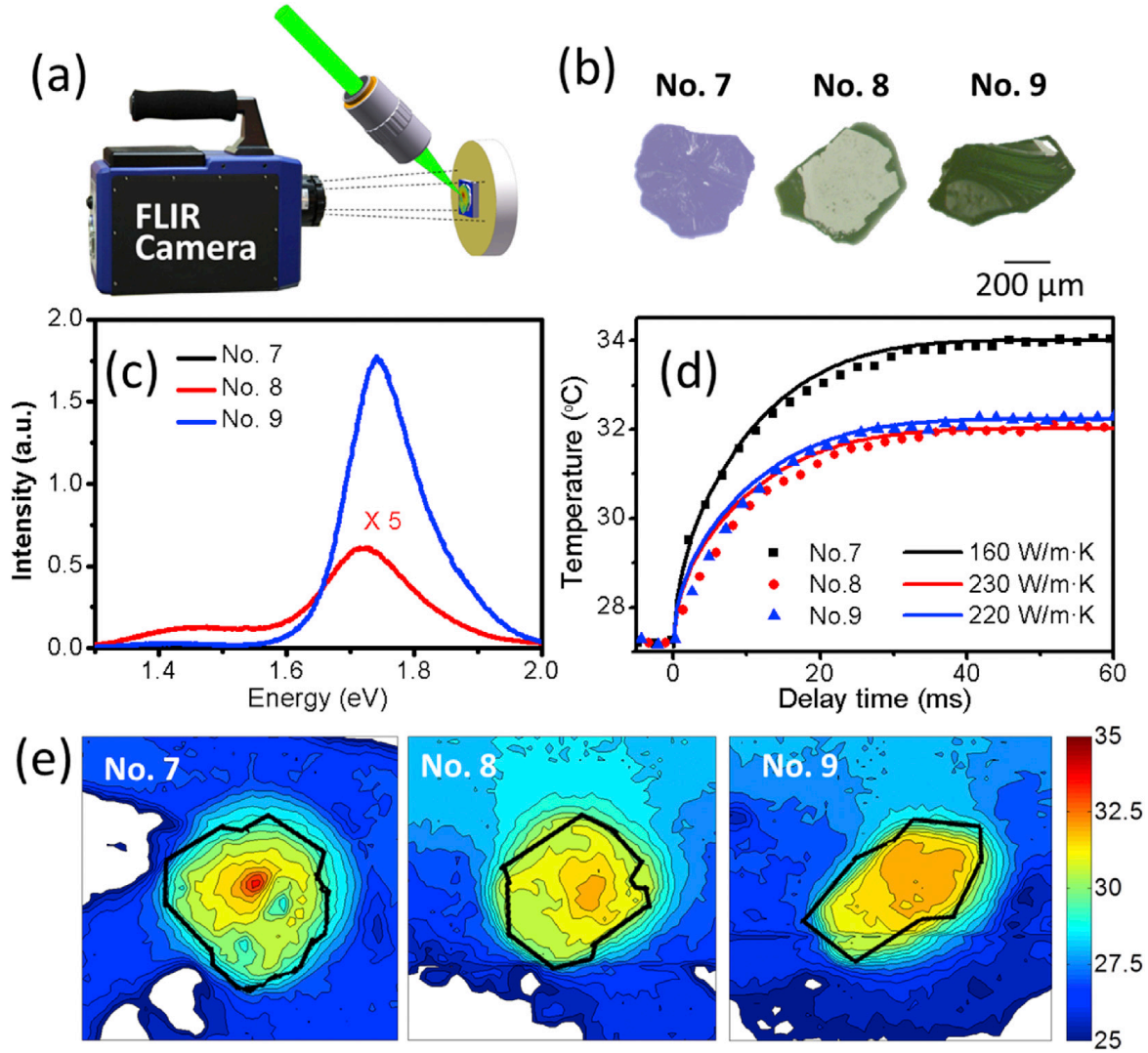


Figure 4.22 Comparison of κ using laser-induced heating and infrared thermal imaging. (a) Schematic of experimental setup. (b) Optical images of three samples. (c) Their PL spectra. The PL of No. 7 was not detected. (d) Temperature evolutions of laser spots (hottest spots in Figure 4.22(e)) on the three samples. Dotted lines are data; the solid lines are COMSOL simulations. Laser was turned on at time zero. (e) Contour map of surface temperatures of the three samples at 40 ms. The heating power of a 532 nm continuous wave (CW) laser is 70 mW.⁶⁵

The failure of the slow thermal camera for high κ materials reminds us of the importance of detection speed; however, it does not mean necessarily that the faster detection speed results in better data. For most heat transport study as demonstrated by TDTP, nanosecond resolution is sufficient and even perfect from the basic physical consideration

because this is the time for photo-excited carriers to fully relax and reach thermal equilibrium with lattice, so that the actual temperature of lattices can be accurately probed by nanosecond PL. This is also true from practical point of view because for samples with thickness on the order of micrometers, the thermal relaxation time is on the order of nanosecond. Ultrafast lasers are required in TDTR mainly because of ultrafast thermal relaxation of the thin metal film thermal transducer.^{57, 81, 93, 94} This thermal relaxation time certainly cannot limit the application of TDTP. For thin films and even atomically thin 2D materials, we can suspend them or place them on a good thermal insulating substrate to eliminate out of plane heat loss. Thus, similar to PL and PL mapping, TDTP can handle most samples, regardless of their size and thickness.

To prove the reliability and accuracy of TDTP, we choose high quality GaAs as a reference to measure its known κ using TDTP. Because its bandgap is lower than that of BAs, the same 527 nm laser will also work for GaAs. Figure 4.23(a) shows the temperature dependent PL spectrum of GaAs. At higher temperatures, the PL of GaAs is dominated by the direct band to-band radiative recombination with energy that follows the temperature dependence of the bandgap. In this case, the total integrated PL intensity is an excellent temperature marker. Figure 4.23(b) shows the integrated PL intensity as a function of temperature measured by the same PMT as for BAs. Based on the TDTP data and simulation in Figure 4.23(c), we obtained a temperature dependent κ of GaAs, as shown in Figure 4.23(d); it agrees well with published values of GaAs,⁹⁵ which firmly proves that our TDTP method is reliable for measuring the κ of BAs.

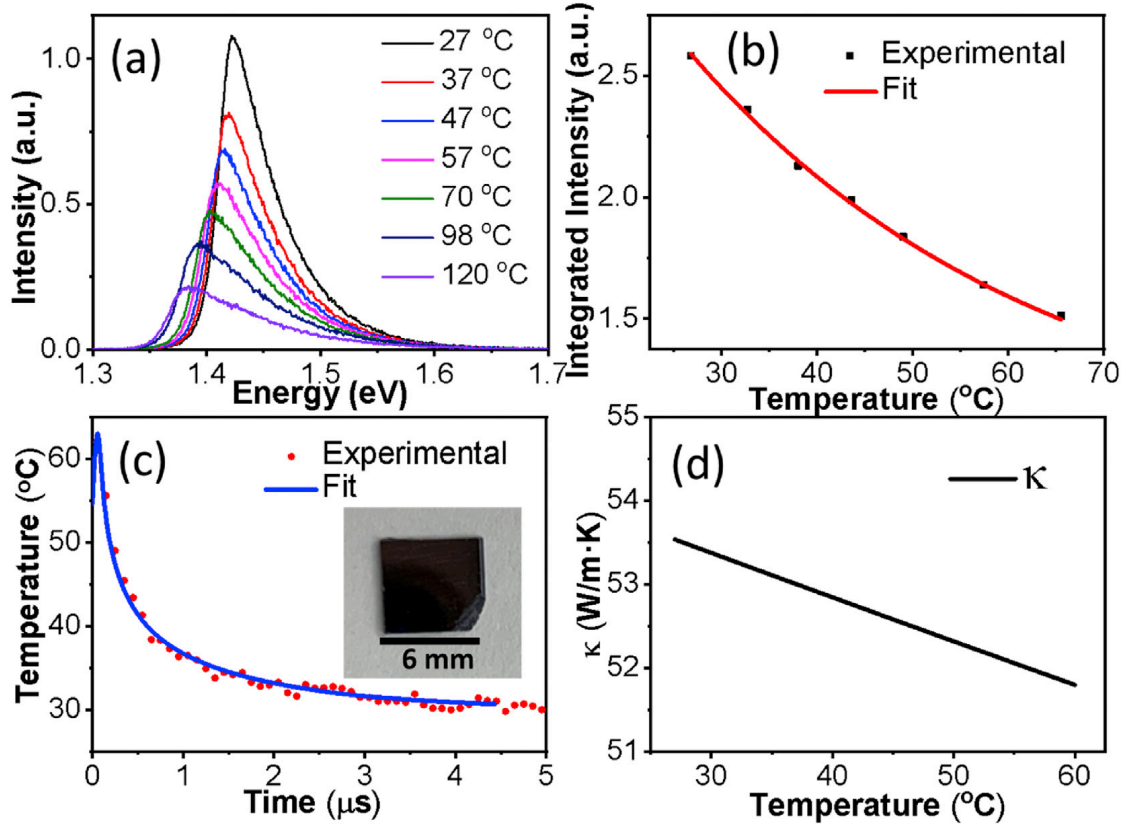


Figure 4.23 Thermal conductivity κ of GaAs measured by TDTP. (a) Temperature-dependent photoluminescence spectrum. (b) Integrated PL intensity as a function of temperature. (c) TDTP trace and simulation. (d) Temperature dependent κ from simulation in (c). TDTP, time-domain thermo-photoluminescence.⁶⁵

Having successfully demonstrated TDTP, we want to stress that TDTP still needs a lot of improvement. Similar to many other optical techniques such as TDTR, there is a lot of room for improvement and refinement that has been going on for many years.⁸¹ For example, the laser pulse width can be reduced to achieve a higher time resolution because of shorter PL lifetimes of BAs and GaAs.⁶⁵ For some materials, the time resolution can be limited by a longer PL lifetime. In any case, it is important to know the response time of PL to achieve an accurate κ especially for materials with high κ . The laser pulse shape and power can be adjusted to make heat generation more accurate and controllable. Similar to PL mapping, TDTP can be optimized and automated to speed up data acquisition and reduce signal

fluctuations. In this demonstration of concept, the experiment was not optimized, and each data were obtained point by point manually; as a result, both temperature calibration and TDTP curves are not smooth, and the simulation fits are also not perfect. However, similar to TDTR, a straightforward analysis of uncertainty is difficult.⁸¹ Experimentally, owing to weaker PL of BAs than GaAs, BAs has a lower quality of TDTP data. Based on preliminary comparisons of simulations and experiments in the supporting materials, as well as the comparison of κ accuracy using GaAs, we believe our measured κ of BAs has a 10 - 15% uncertainty. The essence of combining PL-mapping and TDTP is that it can quickly screen the crystal quality uniformity and find the highest κ value so that researchers can further refine the growth method to achieve crystals with uniformly high κ for any possible applications.

4.5.5 Bandgap Measurement

The optical indirect bandgap was measured using the reflectance and transmittance data measured from UV-visible spectroscopy. First reflectance and transmittance data were measured using thin BAs plate-like samples. Then the absorption coefficient was calculated and the square root of α vs photon energy (Tauc plot), allows us to determine the indirect bandgap. The linear portion of the α which intersects with the x-axis gives the indirect bandgap. Figure 4.24(a) shows the reflectance and transmittance data measured from a UV-visible spectrophotometer (Agilent Cary 5000 Spectrophotometer). The corresponding Tauc plot shown in Figure 4.24(b) which gives the indirect bandgap value close to 2.04 eV for high-quality thin plate-like BAs sample. This data perfectly matched with Song *et al.*'s⁵ recent findings on bandgap measurements using spectroscopic ellipsometry on our BAs samples. He reported the measured indirect bandgap of BAs around 2.02 eV.⁵

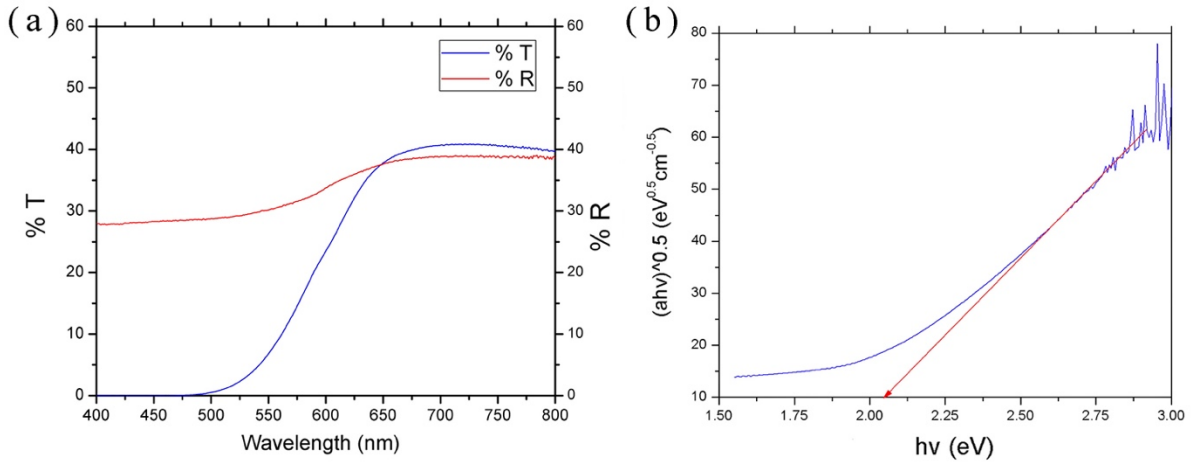


Figure 4.24 (a) Transmittance and reflectance data measured from UV-visible spectrophotometer. (b) The square root of the absorption coefficient of BAs vs photon energy.

4.5.6 Heat Capacity Measurements

Low-temperature heat capacity (C_p) measurement was carried out using Quantum Design PPMS system for the temperature range of 2 - 300 K. Measurement was taken without an external magnetization and room temperature C_p of $34.7 \text{ J mol}^{-1} \text{ K}^{-1}$ was obtained for multiple samples. Figure 4.25 shows the sample attached to the heat capacity puck holder.

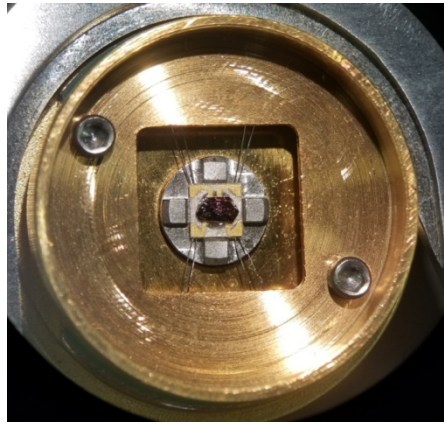


Figure 4.25 BAs sample attached to mounting stations of the heat capacity puck holder using conductive vacuum grease.

Temperature-dependent C_p measurement is very useful for the study of lattice properties, phase transitions and thermodynamic calculations. Hamid *et al.*⁵⁴ performed high-

temperature C_p measurements to calculate enthalpy (H), entropy (S) and Gibbs energy (G) of BAs. Figure 4.26 shows the C_p measurement data in the temperature range of 1.8 – 390 K. PPMS option also have a heating and cooling curve to analyze the first-order phase transitions of the attached samples. No phase transitions were obtained in any of the BAs samples measured using this technique.

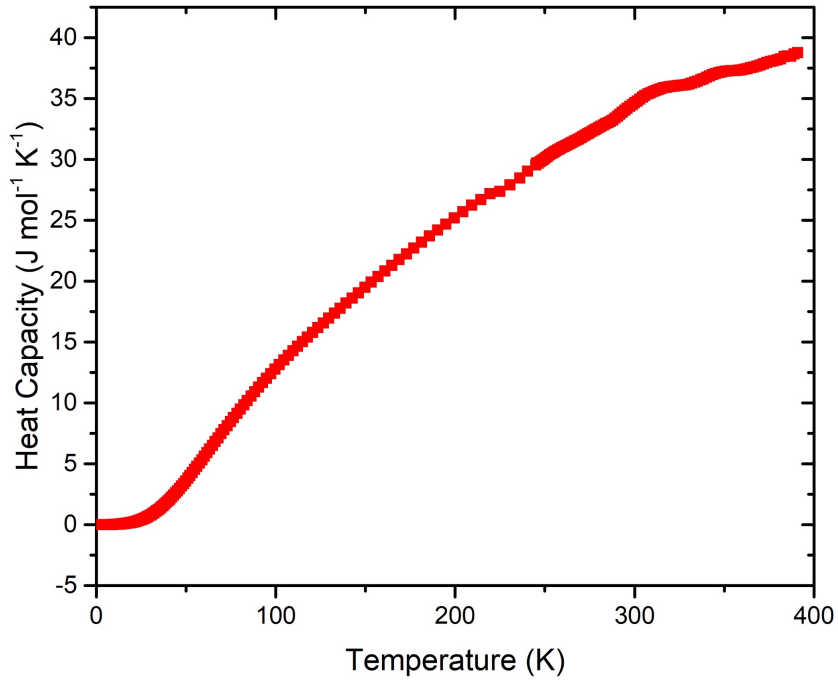


Figure 4.26 Measured C_p data from 1.8 – 300 K.

Furthermore, using the temperature-dependent heat capacity data thermal expansion coefficient (α_l) and Grüneisen parameter (γ) was measured by Chen *et al.*⁹⁶ First temperature dependent lattice parameter of BAs was calculated using XRD analysis data and temperature-dependent thermal expansion coefficient was calculated using second-order polynomial fitting of temperature-dependent lattice parameters. The corresponding measured α_l value at room temperature is $(4.2 \pm 0.4) \times 10^{-6} \text{ K}^{-1}$ and the calculated value using first-principle calculations is $4.0 \times 10^{-6} \text{ K}^{-1}$ at room temperature. The measured γ for BAs is 0.84 ± 0.09 at room

temperature which is in good agreement with the corresponding value of 0.82 calculated from the first principles.⁹⁶ These results indicate that cubic BAs exhibits a much smaller thermal expansion mismatch to common semiconductors compared to diamond and cubic boron nitride. This reduced mismatch is a good advantage that BAs can be used in semiconductor applications with Si and other III-V semiconductor device applications.

4.5.7 Magnetic Property Measurements

Magnetic property measurements were carried out using a vibrating sample magnetometer (VSM) in Quantum Design PPMS system. The BAs sample was attached to the oscillating sample rod using Duco cement, which the amplitude and the position controlled by a linear motor module. Figure 4.27 shows the sample attached to the quartz rod.



Figure 4.27 BAs sample attachment to the quartz holder for VSM measurement.

Figure 4.28(a) and (b) show the $M(T)$ and $M(H)$ measurements on BAs sample shown in Figure 4.27. $M(H)$ was measured under two different temperatures at 50 K and 300 K respectively. Still, it's unclear that the hysteresis loop is shown in $M(H)$ curve is a unique property of BAs or is due to some impurities. But the diamagnetic behavior from $M(T)$ curve is confirmed with many sample measurements, due to negative magnetization at higher

temperatures. Also, there is a transition in the magnetization at low temperatures from negative to positive magnetization.

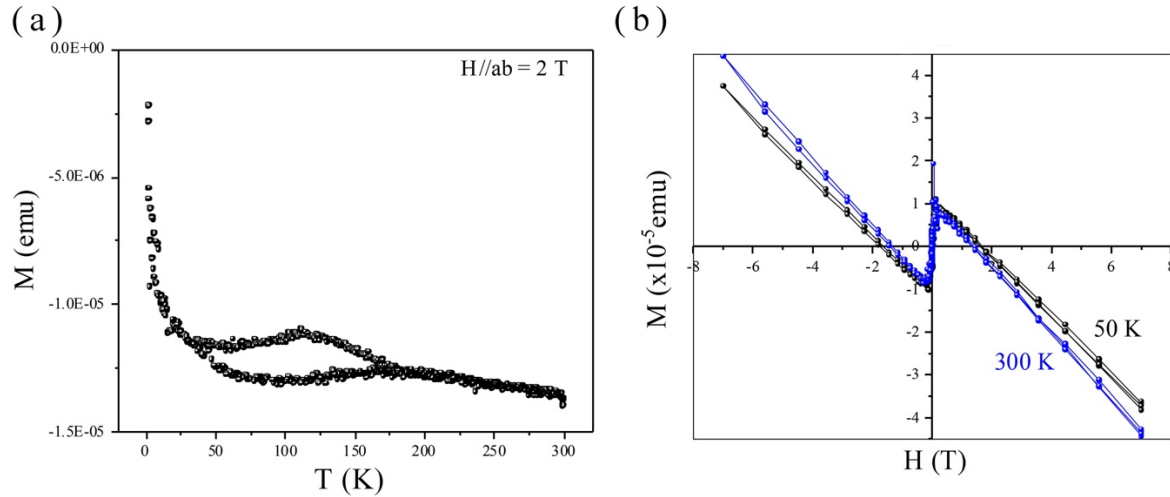


Figure 4.28 $M(T)$ and $M(H)$ measurements of BAs single crystal sample.

4.6 Enhanced CVT Growth

In this part of the project, we focused on further improvements of the CVT growth by avoiding impurities like Si, C, O, etc. Lyons *et al.* predicted that not only native defects but also the group IV impurities like Si, C are strong candidates for the intermediate bandgaps and p-type conductivity.⁷ Based on these predictions we developed some new experiments to avoid such impurities during the CVT process.

4.6.1 C-coating to Avoid Si Impurities

EDX analysis of BAs crystals shows Si impurities in the cross-sections of crystals. Figure 4.29 shows EDX analysis data of BAs samples with Si impurities filled inside a cavity. To avoid the Si impurities mainly carried by fused quartz tubes, we tried to avoid the direct contact between the source materials and the growth end by introducing two methods. As the first method, C-coating was deposited in both the source end and the growth end of the quartz

tube. The same CVT growth process was used with GaAs as the nucleation site. After two weeks, thick plate-like crystals were found, carefully picked, cleaned with *aqua regia*, and ultrasonically bathed to remove contaminants. C-coating somehow prevents the growth of BAs in the inner wall of the quartz tube, but also limited the BAs crystal size.

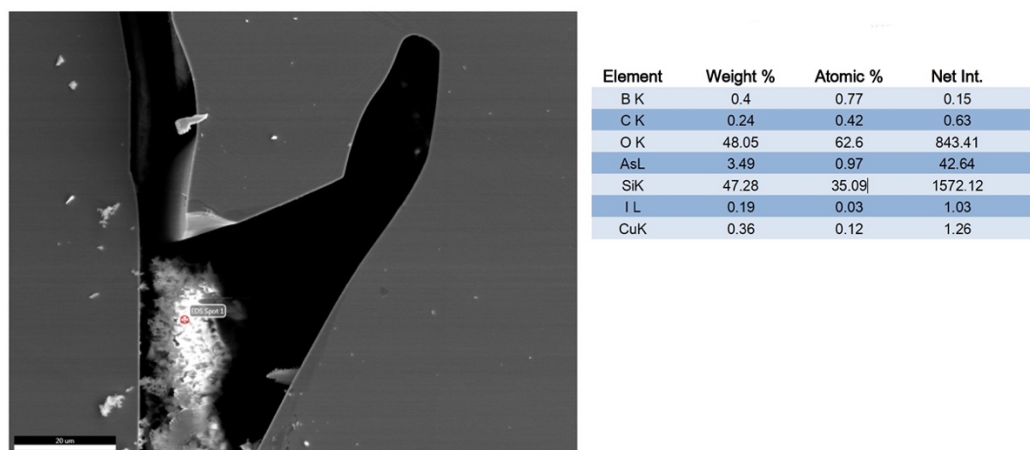


Figure 4.29 SEM/EDX analysis of BAs sample with Si impurities inside a cavity.

Different thermal conductivity values were obtained for the BAs samples grown using c-coated quartz tubes. When the As-site (growth end) is coated maximum room temperature κ of $1290 \text{ W m}^{-1} \text{ K}^{-1}$ was obtained from a thin plate-like BAs sample, while the maximum room temperature κ of $576 \text{ W m}^{-1} \text{ K}^{-1}$ was achieved for the sample grown using C-coating on B-site. Figure 4.30 shows the photographs of BAs single crystals grown using quartz tubes with C-coating on As-site and B-site, respectively and Table 4.6 shows the corresponding κ values for two different samples.

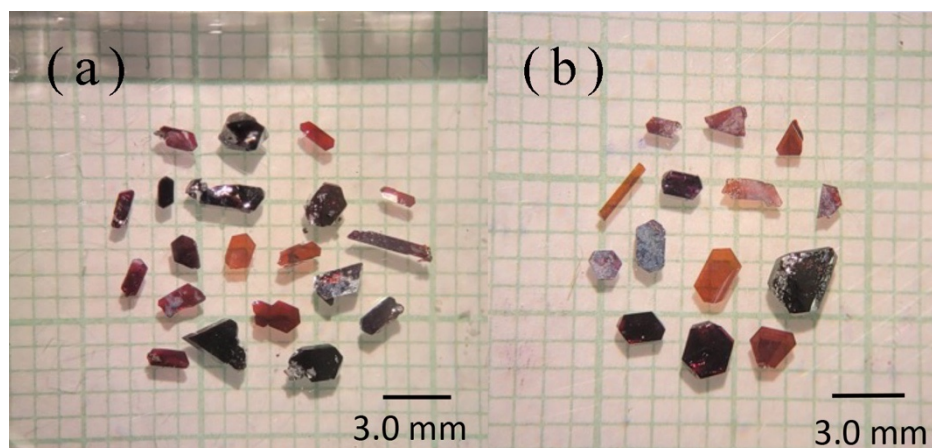


Figure 4.30 Photographs of BAS samples grown using c-coating on (a) As-site and (b) B-site.

Table 4.6 Thermal conductivity data for BAS grown using c-coated quartz tubes from TDTR.

BAs sample	Loc. 1 (W m ⁻¹ K ⁻¹)	Loc. 2 (W m ⁻¹ K ⁻¹)	Loc. 3 (W m ⁻¹ K ⁻¹)	Loc. 4 (W m ⁻¹ K ⁻¹)	Loc. 5 (W m ⁻¹ K ⁻¹)
C-coating on B-site	992	1290	979	1170	1200
C-coating on As-site	193	419	576	491	197

4.6.2 BN Crucible to Avoid C & Si Impurities

As the second method, boron nitride (BN) crucible was introduced to the CVT process. BN crucible (OD – 5 mm, ID – 3 mm) was placed in the growth end of the quartz tube and the same CVT growth process was performed, expecting the growth happens inside the crucible. A short quartz fiber piece was placed inside the crucible as a nucleation site. Due to the size limitations, the crystal growth is very limited and grown crystals are mostly gray thick crystals with a maximum size of 2 mm. Figure 4.31 shows the used BN crucible and the photographs of BAS crystals grown inside the crucible. We were unable to perform any electrical transport measurements on these samples due to size limitations and the shape.

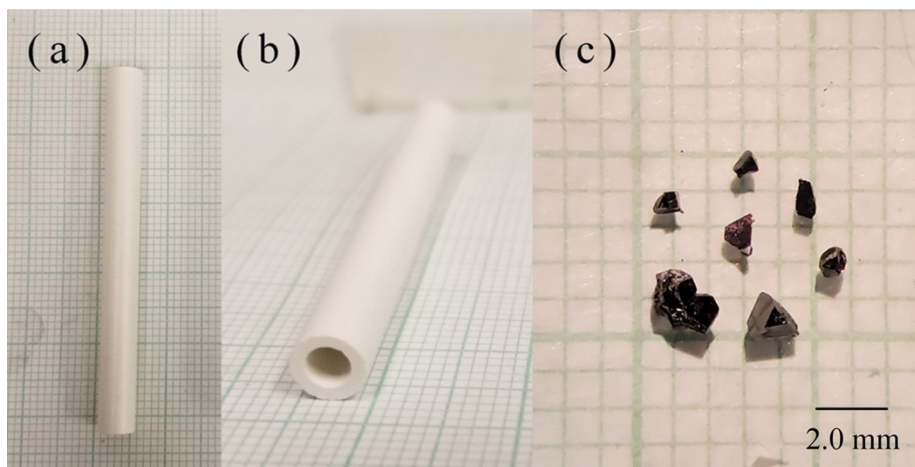


Figure 4.31 BN crucible and the photographs of BA crystals grown inside the crucible.

4.6.3 Purification of Source Materials

Purification of the source material is important to maintain the quality of BA single crystal samples. After careful studies, we found that Si and C impurities mainly coming from the source materials themselves. Therefore, some purification steps were carried out to get pure B and As sources for the CVT growth. As chunks (Alfa Aesar, >99.99999%) was placed in a sealed quartz tube and heat the As side to 800 °C while keeping the other end in much colder temperature. As vaporized and transported to the colder end of the tube. After 48 hrs. almost all the As found recrystallized in the other end of the tube. Some yellow powder residues left on the hot side and later found that to be As_2O_3 . Repeating this step 2 - 3 times can get pure As without any residues left on the hot end of the quartz tube. Figure 4.32(a) shows the schematic setup of the purification process and 4.32(b) shows the yellow color residues left after the recrystallization.

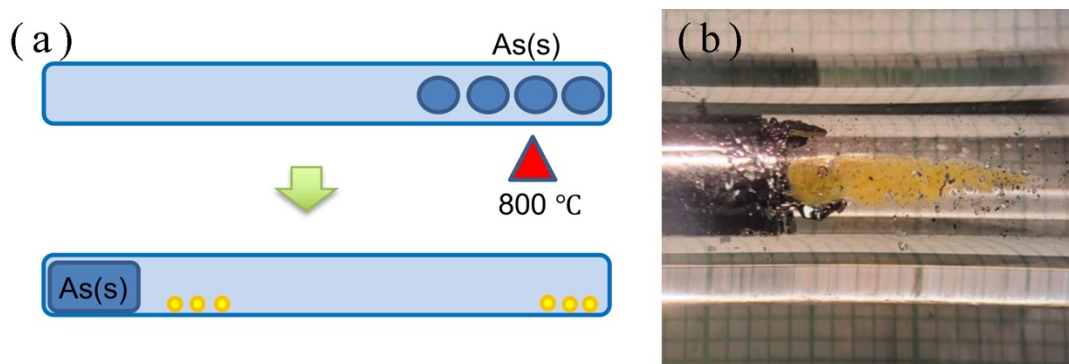


Figure 4.32 (a) Schematic setup of As purification process. (b) As_2O_3 residues left after cool down.

C is a known impurity in our B source, as shown in Figure 4.33 of the chemical analysis report from the suppliers. Therefore, the purification of our B source is becoming very important.

Certificate of Analysis							
Boron Granules 99.9999% Pure							
UMC reference: 14213							
Lot: L000186998							
Impurity	Specification Limit (ppm)	Analytical Results (ppm)	Method	Impurity	Specification Limit (ppm)	Analytical Results (ppm)	Method
Ag	≤0.010	< 0.001	ICP-MS	Li	≤0.100	< 0.005	ICP-MS
Al	≤0.200	0.023	ICP-MS	Mg	≤0.500	< 0.020	ICP-MS
As	≤0.010	< 0.005	ICP-MS	Mn	≤0.025	< 0.003	ICP-MS
Ba	≤0.100	< 0.010	ICP-MS	Mo	≤0.050	< 0.005	ICP-MS
Bi	≤0.040	< 0.004	ICP-MS	Na	≤0.500	< 0.050	ICP-MS
C	≤ 50	< 25	LECO	Ni	≤0.050	0.006	ICP-MS
Ca	≤0.500	< 0.090	ICP-MS	P	≤0.500	< 0.200	ICP-MS
Cd	≤0.100	< 0.010	ICP-MS	Pb	≤0.030	< 0.003	ICP-MS
Co	≤0.020	< 0.002	ICP-MS	Sb	≤0.010	< 0.001	ICP-MS
Cr	≤0.100	< 0.010	ICP-MS	Se	≤0.010	< 0.005	ICP-MS
Cu	≤0.100	0.056	ICP-MS	Si	≤1.000	< 0.500	ICP-MS
Fe	≤0.500	< 0.050	ICP-MS	Sn	≤0.030	< 0.003	ICP-MS
Ga	≤0.070	< 0.005	ICP-MS	Sr	≤0.100	< 0.005	ICP-MS
Ge	≤0.020	< 0.010	ICP-MS	Ti	≤0.050	0.007	ICP-MS
Hg	≤0.010	< 0.005	Hg Analyzer	V	≤0.050	< 0.005	ICP-MS
K	≤0.100	< 0.050	ICP-MS	Zn	≤0.500	< 0.050	ICP-MS

Figure 4.33 Certificate of analysis for high-purity boron source (Alfa Aesar, 99.99999%).

To purify the B, the same CVT process was used with I_2 (Alfa Aesar, >99.999%) and B powder (Alfa Aesar, >99.99999%). Two sources were placed in a sealed quartz tube and heated the source end to 890 °C, while keeping the other end at 780 °C. After 4 weeks, very few amounts of B particles were found to be transported to the cold end of the tube. (Figure 4.34) Due to the high melting point, it is extremely challenging to purify the B source.

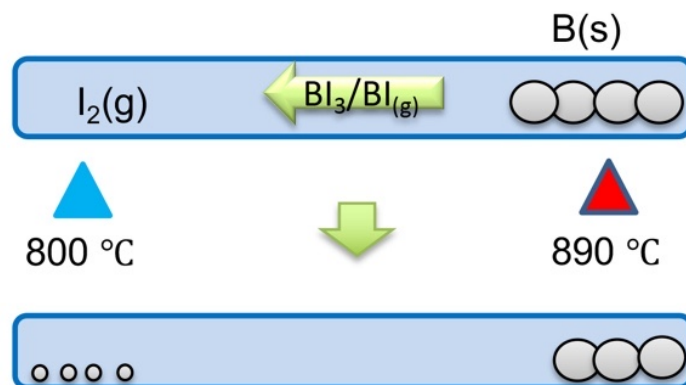


Figure 4.34 Schematic setup of B purification using CVT method. After 4 weeks, only few B particles transfer to the cold end.

Figure 4.35 shows some photographs of the BAs single crystal samples that were grown using a purified As source. Some of the BAs samples from these new batches already obtained room temperature local thermal conductivity above $1200 \text{ W m}^{-1} \text{ K}^{-1}$ and local mobility above $1500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. But still, there is some variation of the thermal conductivity across the same sample, which suggests that despite the improved growth technique and sample quality, some defects may still exist such as surface defects, voids and grains.

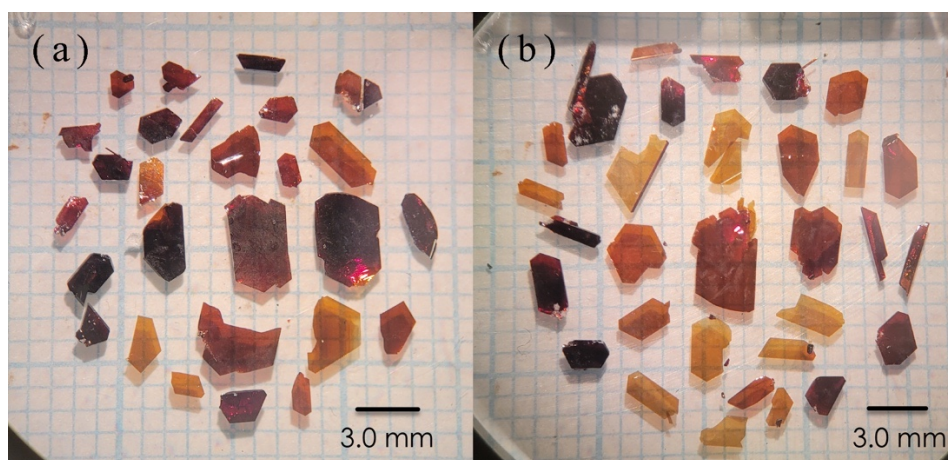


Figure 4.35 Photographs of newly grown high-quality BAs crystals using purified As source.

4.6.4 New Sample Cleaning Technique

Using *aqua regia* is the only known method to clean BAs samples after CVT growth. Recent characterizations found that long exposure to *aqua regia* can damage the surface of BAs single crystals and make some cavities. Figure 4.36 shows the SEM images of delicate surface of BAs after acid washing. There are two main reasons for this kind of cracks and holes to exist in the surface of BAs. One is from the crystal growth itself, combining different factors like impurities and unwanted growth overlapping. The other reason is the use of *aqua regia* to remove excess source materials and impurities that covers the crystals and did some damage to the surface.

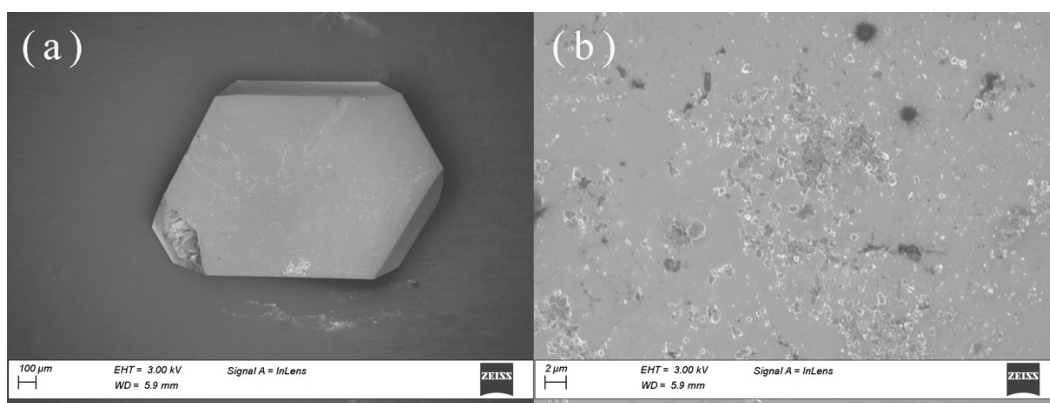


Figure 4.36 SEM images of BAs crystals after cleaning with *aqua regia*. Sample surface shows poor quality with many cracks, holes and irregular facets.

Therefore, we developed a new technique to clean the CVT grown BAs using vaporizations. In the technique, after 2 - 3 weeks of CVT-growth sealed quartz tubes were taken out of the furnace and carefully placed the growth side of the tube at 800 °C for 48 hrs. In that way, all the As covered the grown BAs were transported to the cold side by vaporization and recrystallization. Only the as-grown BAs single crystals remain at the growth side and we can clearly observe where the growth starts. Figure 4.37 shows the before and after cleaning using this vaporization technique of the growth end of the quartz tube.

Most of the red color thin plate-like BAs crystals grown on the quartz fiber and some gray color bulk crystals grown on the inner wall of the tube.

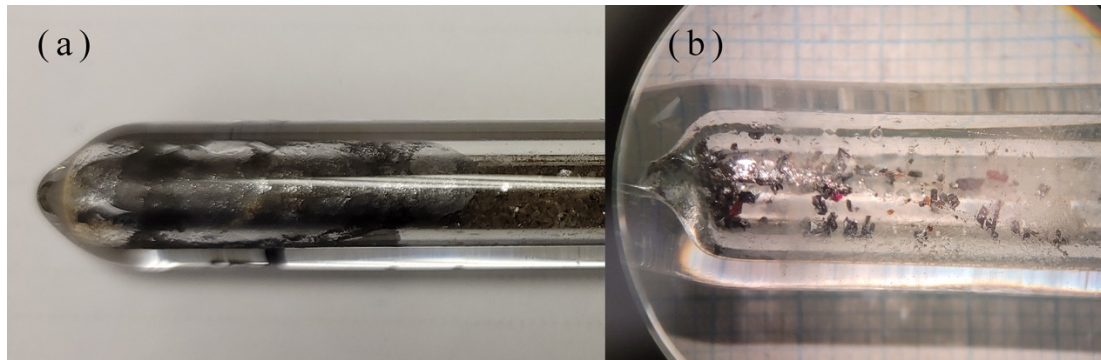


Figure 4.37 (a) Before and (b) after growth end of the quartz tube using new cleaning technique.

Considering the fact that some BAs samples still show poor thermal and electrical properties from the same batch where some BAs achieved the highest thermal conductivity and carrier mobility, there is clearly room to improve the CVT growth with purified sources, nucleation sites and controlled temperature & pressure parameters. The other major issue is the nonuniformity of thermal conductivity in different spots in the same BAs sample, which makes BAs still challenging to use in device applications. In addition, efforts are being made to fully understand the thermodynamic nature of the CVT growth of BAs single crystals.

CHAPTER 5 SUMMARY

Recent theoretical calculations on the group of boron-based cubic III-V compounds reported an ultrahigh room temperature thermal conductivity of $2000 \text{ W m}^{-1} \text{ K}^{-1}$ in boron arsenide (BAs) including only 3-phonon scattering processes. Later adding 3 + 4 phonon processes, researchers calculated the BAs room temperature thermal conductivity close to $1200 \text{ W m}^{-1} \text{ K}^{-1}$. Based on these predictions, I systematically studied the single crystal growth of BAs in this dissertation to prove and realize the exceptional thermal conductivity value which experimentally obtained as the maximum of $1240 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. Except for the single crystal growth, I also enhanced the conventional CVT growth by introducing different nucleation sites and use of optimal growth parameters to grow high-quality BAs with exceptional electrical and thermal properties.

I have been constantly improving the quality of the BAs single crystals by using different sources, nucleation sites, and containers. I found that the limit of the size of BAs growth mainly due to the size of the container. It is key to limit the nucleation numbers to get larger crystals, however, the hetero materials are a source of contamination to affect the κ value. I introduced new nucleation sites that improve the BAs growth and I have grown a 7 mm long BAs single crystal by a nucleation site introduced CVT method. A quartz or GaAs bar, serving as heteronucleation site, is placed at the growth end and helps control the nucleation position and growth direction. By confirming the near-record high room temperature κ value of the obtained crystal by TDTR, we conclude that the introduction of the quartz or GaAs bar provides some control on the nucleation sites of BAs and does not reduce the intrinsic ultrahigh κ .

I have studied the growth of BAs single crystals using different B sources and the experimental comparison clearly shows that using high-quality as-grown BAs as the B source results in faster growth with less impurities. Additionally, if the purity of the raw B can be further improved, BAs single crystals grown by CVT would surely achieve higher thermal conductivity in the future. One last important point is that the observation of the preferred growth direction along the (111) facet of BAs enables nucleation and direction control for the growth. These finds are quite possible to jointly contribute to a more elaborate CVT process and finally result in an industrial-welcome BAs film growth on some selected substrates.

We found a new way to quickly screen the thermal conductivity, which will speed up the search for high κ materials. We have experimentally determined the bandgap of BAs and observed its band-edge PL at room temperature as a measure of crystal quality. We subsequently developed and demonstrated PL mapping and TDTP as quick and reliable screening methods to measure κ values of semiconductors using nanosecond lasers with little sample preparation. Our PL-mapping technique revealed non-uniformity of κ and different κ domains in apparent single crystals BAs, which allowed us to identify the region with highest κ and guide us to improve the growth techniques. TDTP accurately measures the κ of selected spots from the PL mapping images. As rapid non-contact optical techniques with little sample preparation, PL mapping and TDTP will greatly accelerate the search for high κ semiconductors for device applications.

With newly grown high-quality crystals, I measured bandgap of 2.02 eV as predicted, meaning all other gaps are impurity-caused states. Also, the isotope effect of BAs on thermal conductivity is weak, which is extremely important for future applications. I believe my findings will provide insight into determining how to grow larger, better-quality

semiconductor grade BAs single crystals and confirm it as technologically promising material for thermal management applications and also will help establish the foundation for studying and designing BAs-based semiconductor devices.

BIBLIOGRAPHY

1. Lindsay, L.; Broido, D. A.; Reinecke, T. L., First-principles determination of ultrahigh thermal conductivity of boron arsenide: a competitor for diamond? *Physical review letters* **2013**, *111* (2), 025901.
2. Tian, F.; Song, B.; Lv, B.; Sun, J.; Huyan, S.; Wu, Q.; Mao, J.; Ni, Y.; Ding, Z.; Huberman, S.; Liu, T.-H.; Chen, G.; Chen, S.; Chu, C.-W.; Ren, Z., Seeded growth of boron arsenide single crystals with high thermal conductivity. *Applied physics letters* **2018**, *112* (3), 31903.
3. Lv, B.; Lan, Y.; Wang, X.; Zhang, Q.; Hu, Y.; Jacobson, A. J.; Broido, D.; Chen, G.; Ren, Z.; Chu, C.-W., Experimental study of the proposed super-thermal-conductor: BAs. *Applied physics letters* **2015**, *106* (7), 74105.
4. Tian, F.; Song, B.; Chen, X.; Ravichandran, N. K.; Lv, Y.; Chen, K.; Sullivan, S.; Kim, J.; Zhou, Y.; Liu, T.-H.; Goni, M.; Ding, Z.; Sun, J.; Udalamatta Gamage, G. A. G.; Sun, H.; Ziyadee, H.; Huyan, S.; Deng, L.; Zhou, J.; Schmidt, A. J.; Chen, S.; Chu, C.-W.; Huang, P. Y.; Broido, D.; Shi, L.; Chen, G.; Ren, Z., Unusual high thermal conductivity in boron arsenide bulk crystals. *Science* **2018**, *361* (6402), 582.
5. Song, B.; Chen, K.; Bushick, K.; Mengle, K. A.; Tian, F.; Gamage, G. A. G. U.; Ren, Z. F.; Kioupakis, E.; Chen, G., Optical properties of cubic boron arsenide. *Applied Physics Letters* **2020**, *116* (14), 141903.
6. Bushick, K.; Mengle, K.; Sanders, N.; Kioupakis, E., Band structure and carrier effective masses of boron arsenide: Effects of quasiparticle and spin-orbit coupling corrections. *Applied physics letters* **2019**, *114* (2), 22101.

7. Lyons, J. L.; Varley, J. B.; Glaser, E. R.; Freitas, J. A.; Culbertson, J. C.; Tian, F.; Gamage, G. A.; Sun, H.; Ziyadeh, H.; Ren, Z., Impurity-derived p-type conductivity in cubic boron arsenide. *Applied physics letters* **2018**, *113* (25), 251902.
8. Chae, S.; Mengle, K.; Heron, J. T.; Kioupakis, E., Point defects and dopants of boron arsenide from first-principles calculations: Donor compensation and doping asymmetry. *Applied physics letters* **2018**, *113* (21), 212101.
9. Franz, R.; Wiedemann, G., Ueber die Wärme-Leitungsfähigkeit der Metalle. *Annalen der Physik* **1853**, *165* (8), 497-531.
10. Ziman, J. M., *Electrons and phonons; the theory of transport phenomena in solids*. Clarendon Press: Oxford, 1960.
11. Milisavljevic, I.; Wu, Y., Current status of solid-state single crystal growth. *BMC Materials* **2020**, *2* (1), 2.
12. Dhanaraj, G.; Byrappa, K.; Prasad, V.; Dudley, M., *Springer handbook of crystal growth*. Springer, Berlin, Heidelberg: 2010.
13. Pritula, I.; Sangwal, K., 29 - Fundamentals of crystal growth from solutions. In *Handbook of Crystal Growth (Second Edition)*, Rudolph, P., Ed. Elsevier: Boston, 2015; pp 1185-1227.
14. Byrappa, K.; Keerthiraj, N.; Byrappa, S. M., 14 - Hydrothermal growth of crystals—design and processing. In *Handbook of Crystal Growth (Second Edition)*, Rudolph, P., Ed. Elsevier: Boston, 2015; pp 535-575.
15. Wang, J.; Zhang, G.; Yu, H.; Wang, Y.; Chen, C., 5 - Czochralski and flux growth of crystals for lasers and nonlinear optics. In *Handbook of Crystal Growth (Second Edition)*, Rudolph, P., Ed. Elsevier: Boston, 2015; pp 169-208.

16. Friedrich, J.; von Ammon, W.; Müller, G., 2 - Czochralski growth of silicon crystals. In *Handbook of Crystal Growth (Second Edition)*, Rudolph, P., Ed. Elsevier: Boston, 2015; pp 45-104.
17. Muiznieks, A.; Virbulis, J.; Lüdge, A.; Riemann, H.; Werner, N., 7 - Floating zone growth of silicon. In *Handbook of Crystal Growth (Second Edition)*, Rudolph, P., Ed. Elsevier: Boston, 2015; pp 241-279.
18. Jurisch, M.; Eichler, S.; Bruder, M., 9 - Vertical bridgman growth of binary compound semiconductors. In *Handbook of Crystal Growth (Second Edition)*, Rudolph, P., Ed. Elsevier: Boston, 2015; pp 331-372.
19. Schmidt, P.; Binnewies, M.; Glaum, R.; Schmidt, M. In *Chemical vapor transport reactions methods, materials, modeling*, 2013.
20. Schäfer, H., *Chemical transport reactions*. Elsevier: 1964.
21. Streetman, B.; Banerjee, S., *Solid state electronic devices*. Seventh Edition ed.; Pearson, Boston: 2016.
22. Kawamura, T.; Hori, D.; Kangawa, Y.; Kakimoto, K.; Yoshimura, M.; Mori, Y., Thermal conductivity of SiC calculated by molecular dynamics. *Japanese Journal of Applied Physics* **2008**, 47 (12), 8898-8901.
23. Gamage, G. A.; Sun, H.; Ziyadeh, H.; Tian, F.; Ren, Z., Effect of boron sources on the growth of boron arsenide single crystals by chemical vapor transport. *Applied physics letters* **2019**, 115 (9), 92103.
24. Moore, A. L.; Shi, L., Emerging challenges and materials for thermal management of electronics. *Materials today (Kidlington, England)* **2014**, 17 (4), 163-174.

25. Slack, G. A., Nonmetallic crystals with high thermal conductivity. *The Journal of physics and chemistry of solids* **1973**, 34 (2), 321-335.
26. Han, Z.; Fina, A., Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review. *Progress in polymer science* **2011**, 36 (7), 914-944.
27. Palyanov, Y. N.; Kupriyanov, I. N.; Khokhryakov, A. F.; Ralchenko, V. G., 17 - Crystal growth of diamond. In *Handbook of Crystal Growth (Second Edition)*, Rudolph, P., Ed. Elsevier: Boston, 2015; pp 671-713.
28. Bundy, F. P.; Hall, H. T.; Strong, H. M.; Wentorfjun, R. H., Man-made diamonds. *Nature* **1955**, 176 (4471), 51-55.
29. Wang, L.-F.; Zheng, Q.-S., Extreme anisotropy of graphite and single-walled carbon nanotube bundles. *Applied physics letters* **2007**, 90 (15), 153113-153113-3.
30. Loos, M., Chapter 3 - Allotropes of carbon and carbon nanotubes. In *Carbon Nanotube Reinforced Composites*, Loos, M., Ed. William Andrew Publishing: Oxford, 2015; pp 73-101.
31. Yu, C.; Shi, L.; Yao, Z.; Li, D.; Majumdar, A., Thermal conductance and thermopower of an lindividual single-wall carbon nanotube. *Nano letters* **2005**, 5 (9), 1842-1846.
32. Kim, P.; Shi, L.; Majumdar, A.; McEuen, P. L., Thermal transport measurements of individual multiwalled nanotubes. *Physical review letters* **2001**, 87 (21), 215502-215502.
33. Chen, K.; Song, B.; Ravichandran, N. K.; Zheng, Q.; Chen, X.; Lee, H.; Sun, H.; Li, S.; Udalamatta Gamage, G. A. G.; Tian, F.; Ding, Z.; Song, Q.; Rai, A.; Wu, H.; Koirala, P.; Schmidt, A. J.; Watanabe, K.; Lv, B.; Ren, Z.; Shi, L.; Cahill, D. G.; Taniguchi, T.; Broido, D.; Chen, G., Ultrahigh thermal conductivity in isotope-enriched cubic

boron nitride. *Science (American Association for the Advancement of Science)* **2020**, 367 (6477), 555-559.

34. Broido, D. A.; Lindsay, L.; Reinecke, T. L., Ab initio study of the unusual thermal transport properties of boron arsenide and related materials. *Physical review. B, Condensed matter and materials physics* **2013**, 88 (21).

35. Onn, D. G.; Witek, A.; Qiu, Y. Z.; Anthony, T. R.; Banholzer, W. F., Some aspects of the thermal conductivity of isotopically enriched diamond single crystals. *Physical review letters* **1992**, 68 (18), 2806-2809.

36. Olson, J. R.; Pohl, R. O.; Vandersande, J. W.; Zoltan, A.; Anthony, T. R.; Banholzer, W. F., Thermal conductivity of diamond between 170 and 1200 K and the isotope effect. *Physical review. B, Condensed matter* **1993**, 47 (22), 14850-14856.

37. Lanhua, W. E. I.; Kuo, P. K.; Thomas, R. L.; Anthony, T. R.; Banholzer, W. F., Thermal conductivity of isotopically modified single crystal diamond. *Physical review letters* **1993**, 70 (24), 3764-3767.

38. Berman, R.; Hudson, P. R. W.; Martinez, M., Nitrogen in diamond: evidence from thermal conductivity. *Journal of physics. C, Solid state physics* **1975**, 8 (21), L430-L434.

39. Kumashiro, Y.; Mitsuhashi, T.; Okaya, S.; Muta, F.; Koshiro, T.; Takahashi, Y.; Mirabayashi, M., Thermal conductivity of a boron phosphide single-crystal wafer up to high temperature. *Journal of applied physics* **1989**, 65 (5), 2147-2148.

40. Slack, G. A.; Schowalter, L. J.; Morelli, D.; Freitas, J. A., Some effects of oxygen impurities on AlN and GaN. *Journal of crystal growth* **2002**, 246 (3), 287-298.

41. Slack, G. A.; Tanzilli, R. A.; Pohl, R. O.; Vandersande, J. W., The intrinsic thermal conductivity of AlN. *The Journal of physics and chemistry of solids* **1987**, 48 (7), 641-647.

42. Slack, G. A., Thermal conductivity of pure and impure silicon, silicon carbide, and diamond. *Journal of applied physics* **1964**, 35 (12), 3460-3466.
43. Greene, R. G.; Luo, H.; Ruoff, A. L.; Trail, S. S.; DiSalvo, J. F. J., Pressure induced metastable amorphization of BAs: Evidence for a kinetically frustrated phase transformation. *Physical review letters* **1994**, 73 (18), 2476-2479.
44. Feng, T.; Lindsay, L.; Ruan, X., Four-phonon scattering significantly reduces intrinsic thermal conductivity of solids. *Physical review. B* **2017**, 96 (16).
45. Maradudin, A. A.; Fein, A. E., Scattering of neutrons by an anharmonic crystal. *Physical review* **1962**, 128 (6), 2589-2608.
46. Liu, T.-H.; Song, B.; Meroueh, L.; Ding, Z.; Song, Q.; Zhou, J.; Li, M.; Chen, G., Simultaneously high electron and hole mobilities in cubic boron-V compounds: BP, BAs, and BSb. *Physical review. B* **2018**, 98 (8).
47. Sun, J.; Kosel, J. In *Finite-element modelling and analysis of hall effect and extraordinary magnetoresistance effect*, 2012.
48. Santos, T. G., 5 - Characterization of FSP by electrical conductivity. Elsevier Ltd: 2014; pp 153-176.
49. Demichelis, F.; Kaniadakis, G.; Tagliaferro, A.; Tresso, E., New approach to optical analysis of absorbing thin solid films. *Applied Optics* **1987**, 26 (9), 1737-1740.
50. Pankove, J. I., *Optical processes in semiconductors*. Prentice-Hall: Englewood Cliffs, N.J, 1971.
51. Rosencher, E.; Vinter, B., *Optoelectronics*. Cambridge University Press: Cambridge, 2002.

52. Woollam, J. A.; Johs, B. D.; Herzinger, C. M.; Hilfiker, J. N.; Synowicki, R. A.; Bungay, C. L., Overview of variable-angle spectroscopic ellipsometry (VASE): I. Basic theory and typical applications. SPIE: 1999; Vol. 10294, pp 1029402-1029402-26.
53. Tauc, J.; Menth, A., States in the gap. *Journal of Non-Crystalline Solids* **1972**, 8-10, 569-585.
54. Ziyadee, H.; Gamage, G. A.; Sun, H.; Tian, F.; Ren, Z., Thermodynamic calculation and its experimental correlation with the growth process of boron arsenide single crystals. *Journal of applied physics* **2019**, 126 (15), 155108.
55. Parker, W. J.; Jenkins, R. J.; Butler, C. P.; Abbott, G. L., Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity. *Journal of applied physics* **1961**, 32 (9), 1679-1684.
56. Cahill, D. G.; Pohl, R. O., Thermal conductivity of amorphous solids above the plateau. *Physical review. B, Condensed matter* **1987**, 35 (8), 4067-4073.
57. Jiang, P.; Qian, X.; Yang, R., Tutorial: Time-domain thermoreflectance (TDTR) for thermal property characterization of bulk and thin film materials. *Journal of applied physics* **2018**, 124 (16), 161103.
58. Schmidt, A. J.; Chen, X.; Chen, G., Pulse accumulation, radial heat conduction, and anisotropic thermal conductivity in pump-probe transient thermoreflectance. *Review of scientific instruments* **2008**, 79 (11), 114902-114902-9.
59. Cahill, D. G., Analysis of heat flow in layered structures for time-domain thermoreflectance. *Review of scientific instruments* **2004**, 75 (12), 5119-5122.
60. Cahill, D. G.; Braun, P. V.; Chen, G.; Clarke, D. R.; Fan, S.; Goodson, K. E.; Keblinski, P.; King, W. P.; Mahan, G. D.; Majumdar, A.; Maris, H. J.; Phillpot, S. R.;

Pop, E.; Shi, L., Nanoscale thermal transport. II. 2003–2012. *Applied Physics Reviews* **2014**, *1* (1), 11305.

61. Feldman, A., Algorithm for solutions of the thermal diffusion equation in a satisfied medium with a modulated heating source. *High Temperatures - High Pressures* **1999**, *31* (3), 293-298.

62. Carslaw, H. S.; Jaeger, J. C.; Lienhard, J. H., *Conduction of heat in solids*. Second edition. ed.; Clarendon Press: Oxford, 1959.

63. Schmidt, A.; Chiesa, M.; Chen, X.; Chen, G., An optical pump-probe technique for measuring the thermal conductivity of liquids. *Review of scientific instruments* **2008**, *79* (6), 064902-064902.

64. Sun, H.; Chen, K.; Gamage, G. A.; Ziyadeh, H.; Wang, F.; Wang, Y.; Hadjiev, V. G.; Tian, F.; Chen, G.; Ren, Z., Boron isotope effect on the thermal conductivity of boron arsenide single crystals. *Materials Today Physics* **2019**, *11*, 100169.

65. Yue, S.; Gamage, G. A.; Mohebinia, M.; Mayerich, D.; Talari, V.; Deng, Y.; Tian, F.; Dai, S. Y.; Sun, H.; Hadjiev, V. G.; Zhang, W.; Feng, G.; Hu, J.; Liu, D.; Wang, Z.; Ren, Z.; Bao, J., Photoluminescence mapping and time-domain thermo-photoluminescence for rapid imaging and measurement of thermal conductivity of boron arsenide. *Materials Today Physics* **2020**, *13*, 100194.

66. Hadjiev, V. G.; Iliev, M. N.; Lv, B.; Ren, Z. F.; Chu, C. W., Anomalous vibrational properties of cubic boron arsenide. *Physical review. B, Condensed matter and materials physics* **2014**, *89* (2).

67. Chu, T. L.; Hyslop, A. E., Crystal growth and properties of boron monoarsenide. *Journal of applied physics* **1972**, *43* (2), 276-279.

68. Perri, J. A.; Placa, S. L.; Post, B., New group III-group V compounds: BP and BAs. *Acta Crystallographica* **1958**, *11*, 310.
69. Xing, J.; Glaser, E. R.; Song, B.; Culbertson, J. C.; Freitas, J. A.; Duncan, R. A.; Nelson, K. A.; Chen, G.; Ni, N., Gas-pressure chemical vapor transport growth of millimeter-sized c-BAs single crystals with moderate thermal conductivity. *Applied physics letters* **2018**, *112* (24), 241903.
70. Xing, J.; Chen, X.; Zhou, Y.; Culbertson, J. C.; Freitas, J. A.; Glaser, E. R.; Zhou, J.; Shi, L.; Ni, N., Multimillimeter-sized cubic boron arsenide grown by chemical vapor transport via a tellurium tetraiodide transport agent. *Applied physics letters* **2018**, *112* (26), 261901.
71. Landolt, H.; Börnstein, R., *Phase equilibria, crystallographic and thermodynamic data of binary alloys*. Springer-Verlag: 1993; Vol. 3.
72. Portnoi, K. I.; Romashov, V. M.; Chubarov, V. M.; Levinskaya, M. K.; Salibekov, S. E., Phase diagram of the system nickel-boron. *Soviet Powder Metallurgy and Metal Ceramics* **1967**, *6* (2), 99-103.
73. Kumashiro, Y.; Yao, T.; Gonda, S., Crystal growth of boron phosphide by high pressure flux method. *Journal of crystal growth* **1984**, *70* (1), 515-518.
74. Dumont, H.; Monteil, Y., Some aspects on thermodynamic properties, phase diagram and alloy formation in the ternary system BAs–GaAs—Part I: Analysis of BAs thermodynamic properties. *Journal of crystal growth* **2006**, *290* (2), 410-418.
75. Tian, F.; Ren, Z., High thermal conductivity in boron arsenide: From prediction to reality. *Angewandte Chemie (International ed.)* **2019**, *58* (18), 5824-5831.

76. Li, S.; Zheng, Q.; Lv, Y.; Liu, X.; Wang, X.; Huang, P. Y.; Cahill, D. G.; Lv, B., High thermal conductivity in cubic boron arsenide crystals. *Science (American Association for the Advancement of Science)* **2018**, *361* (6402), 579-581.
77. Kang, J. S.; Li, M.; Wu, H.; Nguyen, H.; Hu, Y., Experimental observation of high thermal conductivity in boron arsenide. *Science (American Association for the Advancement of Science)* **2018**, *361* (6402), 575-578.
78. Cueilleron, J.; Viala, J. C., Direct synthesis of boron triiodide and the chemical transport of boron with iodine. *Journal of the Less Common Metals* **1978**, *58* (2), 123-131.
79. Gamage, G. A.; Chen, K.; Chen, G.; Tian, F.; Ren, Z., Effect of nucleation sites on the growth and quality of single-crystal boron arsenide. *Materials Today Physics* **2019**, *11*, 100160.
80. Bean, K. E.; Gleim, P. S., The influence of crystal orientation on silicon semiconductor processing. *Proceedings of the IEEE* **1969**, *57* (9), 1469-1476.
81. Yang, J.; Ziade, E.; Schmidt, A. J., Uncertainty analysis of thermoreflectance measurements. *Review of scientific instruments* **2016**, *87* (1), 014901-014901.
82. Zheng, Q.; Polanco, C. A.; Du, M.-H.; Lindsay, L. R.; Chi, M.; Yan, J.; Sales, B. C., Antisite pairs suppress the thermal conductivity of BAs. *Physical review letters* **2018**, *121* (10), 105901-105901.
83. SchÄFer, H., CHAPTER 5 - Chemical transport processes as an aid in preparative chemistry. Combination of transport reactions with other processes. In *Chemical Transport Reactions*, SchÄFer, H., Ed. Academic Press: 1964; pp 115-131.

84. SchÄFer, H., CHAPTER 3 - The transport of solid substances and its special applications. In *Chemical Transport Reactions*, SchÄFer, H., Ed. Academic Press: 1964; pp 35-98.
85. Carlson, R. O.; Slack, G. A.; Silverman, S. J., Thermal conductivity of GaAs and GaAs_{1-x}P_x laser semiconductors. *Journal of applied physics* **1965**, 36 (2), 505-507.
86. Buckeridge, J.; Scanlon, D. O., Electronic band structure and optical properties of boron arsenide. *Physical Review Materials* **2019**, 3 (5), 051601.
87. Hart, G. L. W.; Zunger, A., Electronic structure of BAs and boride III-V alloys. *Physical review. B, Condensed matter* **2000**, 62 (20), 13522-13537.
88. Ferhat, M.; Zaoui, A.; Certier, M.; Aourag, H., Electronic structure of BN, BP and BAs. *Physica. B, Condensed matter* **1998**, 252 (3), 229-236.
89. Wang, S.; Swingle, S. F.; Ye, H.; Fan, F.-R. F.; Cowley, A. H.; Bard, A. J., Synthesis and characterization of a p-type boron arsenide photoelectrode. *Journal of the American Chemical Society* **2012**, 134 (27), 11056-11059.
90. Chu, T. L.; Hyslop, A. E., Preparation and properties of boron arsenide films. *Journal of the Electrochemical Society* **1974**, 121 (3), 412.
91. Ku, S. M., Preparation and properties of boron arsenides and boron arsenide-gallium arsenide mixed crystals. *Journal of The Electrochemical Society* **1966**, 113 (8), 813.
92. Yu, P. Y.; Cardona, M., *Fundamentals of semiconductors : physics and materials properties*. 4th ed. ed.; Springer: Berlin ;, 2010.
93. Zhao, D.; Qian, X.; Gu, X.; Jajja, S. A.; Yang, R., Measurement techniques for thermal conductivity and interfacial thermal conductance of bulk and thin film materials. **2016**.

94. Cahill, D. G.; Fischer, H. E.; Klitsner, T.; Swartz, E. T.; Pohl, R. O., Thermal conductivity of thin films: Measurements and understanding. *Journal of vacuum science & technology. A, Vacuum, surfaces, and films* **1989**, 7 (3), 1259-1266.
95. Blakemore, J. S., Semiconducting and other major properties of gallium arsenide. *Journal of applied physics* **1982**, 53 (10), R123-R181.
96. Chen, X.; Li, C.; Tian, F.; Gamage, G. A.; Sullivan, S.; Zhou, J.; Broido, D.; Ren, Z.; Shi, L., Thermal expansion coefficient and lattice anharmonicity of cubic boron arsenide. *Physical review applied* **2019**, 11 (6).

LIST OF PUBLICATIONS

1. Stevens, D. L.; Ortiz, A.; Cho, C.; Gamage, G. A.; Ren, Z.; Grunlan, J. C., Cation Size influence on the power factor of salt-doped organic nanocomposite thin films. *(Submitted)* **2021**.
2. Lee, H.; Gamage, G. A.; Lyons, J. L.; Tian, F.; Smith, B.; Glaser, E. R.; Ren, Z.; Shi, L., Electronic structure of cubic boron arsenide probed by scanning tunneling spectroscopy. *(Submitted)* **2021**.
3. Yue, S.*; Gamage, G. A.*; Mohebinia, M.; Mayerich, D.; Talari, V.; Deng, Y.; Tian, F.; Dai, S. Y.; Sun, H.; Hadjiev, V. G.; Zhang, W.; Feng, G.; Hu, J.; Liu, D.; Wang, Z.; Ren, Z.; Bao, J., Photoluminescence mapping and time-domain thermophotoluminescence for rapid imaging and measurement of thermal conductivity of boron arsenide. *Materials Today Physics* **2020**, *13*, 100194.
4. Stevens, D. L.; Gamage, G. A.; Ren, Z.; Grunlan, J. C., Salt doping to improve thermoelectric power factor of organic nanocomposite thin films. *RSC Advances* **2020**, *10* (20), 11800-11807.
5. Song, B.; Chen, K.; Bushick, K.; Mengle, K. A.; Tian, F.; Gamage, G. A. G. U.; Ren, Z. F.; Kioupakis, E.; Chen, G., Optical properties of cubic boron arsenide. *Applied Physics Letters* **2020**, *116* (14), 141903.
6. Ren, W.; Song, Q.; Zhu, H.; Mao, J.; You, L.; Gamage, G. A.; Zhou, J.; Zhou, T.; Jiang, J.; Wang, C.; Luo, J.; Wu, J.; Wang, Z.; Chen, G.; Ren, Z., Intermediate-level doping strategy to simultaneously optimize power factor and phonon thermal conductivity for improving thermoelectric figure of merit. *Materials Today Physics* **2020**, *15*, 100250.

7. Chen, K.; Song, B.; Ravichandran, N. K.; Zheng, Q.; Chen, X.; Lee, H.; Sun, H.; Li, S.; Udalamattha Gamage, G. A. G.; Tian, F.; Ding, Z.; Song, Q.; Rai, A.; Wu, H.; Koirala, P.; Schmidt, A. J.; Watanabe, K.; Lv, B.; Ren, Z.; Shi, L.; Cahill, D. G.; Taniguchi, T.; Broido, D.; Chen, G., Ultrahigh thermal conductivity in isotope-enriched cubic boron nitride. *Science (American Association for the Advancement of Science)* **2020**, 367 (6477), 555-559.
8. Ziyadee, H.; Gamage, G. A.; Sun, H.; Tian, F.; Ren, Z., Thermodynamic calculation and its experimental correlation with the growth process of boron arsenide single crystals. *Journal of applied physics* **2019**, 126 (15), 155108.
9. Tian, F.; Luo, K.; Xie, C.; Liu, B.; Liang, X.; Wang, L.; Gamage, G. A.; Sun, H.; Ziyadee, H.; Sun, J.; Zhao, Z.; Xu, B.; Gao, G.; Zhou, X.-F.; Ren, Z., Mechanical properties of boron arsenide single crystal. *Applied physics letters* **2019**, 114 (13), 131903.
10. Sun, H.; Chen, K.; Gamage, G. A.; Ziyadee, H.; Wang, F.; Wang, Y.; Hadjiev, V. G.; Tian, F.; Chen, G.; Ren, Z., Boron isotope effect on the thermal conductivity of boron arsenide single crystals. *Materials Today Physics* **2019**, 11, 100169.
11. Mao, J.; Zhu, H.; Ding, Z.; Liu, Z.; Gamage, G. A.; Chen, G.; Ren, Z., High thermoelectric cooling performance of n-type Mg₃Bi₂-based materials. *Science (American Association for the Advancement of Science)* **2019**, 365 (6452), 495-498.
12. Gamage, G. A.; Sun, H.; Ziyadee, H.; Tian, F.; Ren, Z., Effect of boron sources on the growth of boron arsenide single crystals by chemical vapor transport. *Applied physics letters* **2019**, 115 (9), 92103.

13. Gamage, G. A.; Chen, K.; Chen, G.; Tian, F.; Ren, Z., Effect of nucleation sites on the growth and quality of single-crystal boron arsenide. *Materials Today Physics* **2019**, *11*, 100160.
14. Chen, X.; Li, C.; Tian, F.; Gamage, G. A.; Sullivan, S.; Zhou, J.; Broido, D.; Ren, Z.; Shi, L., Thermal expansion coefficient and lattice anharmonicity of cubic boron arsenide. *Physical review applied* **2019**, *11* (6), 64070.
15. Tian, F.; Song, B.; Chen, X.; Ravichandran, N. K.; Lv, Y.; Chen, K.; Sullivan, S.; Kim, J.; Zhou, Y.; Liu, T.-H.; Goni, M.; Ding, Z.; Sun, J.; Udalamatta Gamage, G. A. G.; Sun, H.; Ziyatee, H.; Huyan, S.; Deng, L.; Zhou, J.; Schmidt, A. J.; Chen, S.; Chu, C.-W.; Huang, P. Y.; Broido, D.; Shi, L.; Chen, G.; Ren, Z., Unusual high thermal conductivity in boron arsenide bulk crystals. *Science* **2018**, *361* (6402), 582.
16. Lyons, J. L.; Varley, J. B.; Glaser, E. R.; Freitas, J. A.; Culbertson, J. C.; Tian, F.; Gamage, G. A.; Sun, H.; Ziyatee, H.; Ren, Z., Impurity-derived p-type conductivity in cubic boron arsenide. *Applied physics letters* **2018**, *113* (25), 251902.