Seeded growth of boron arsenide single crystals with high thermal conductivity

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

Citation

As Published
http://dx.doi.org/10.1063/1.5004200

Publisher
AIP Publishing

Version
Final published version

Accessed
Thu Apr 11 04:28:38 EDT 2019

Citable Link
http://hdl.handle.net/1721.1/120513

Terms of Use
Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.

Detailed Terms
Seeded growth of boron arsenide single crystals with high thermal conductivity

Fei Tian,1 Bai Song,2 Bing Lv,3 Jingying Sun,1 Shuyuan Huyan,1 Qi Wu,1 Jun Mao,1,4 Yizhou Ni,1 Zhiwei Ding,2 Samuel Huberman,2 Te-Huan Liu,2 Gang Chen,2 Shuo Chen,1 Ching-Wu Chu,1 and Zhifeng Ren1(a)

1Department of Physics and the Texas Center for Superconductivity, University of Houston, Houston, Texas 77204, USA
2Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
3Department of Physics, University of Texas at Dallas, Dallas, Texas 75080, USA
4Department of Mechanical Engineering, University of Houston, Houston, Texas 77204, USA

(Received 12 September 2017; accepted 29 December 2017; published online 16 January 2018)

Materials with high thermal conductivities are crucial to effectively cooling high-power-density electronic and optoelectronic devices. Recently, zinc-blende boron arsenide (BAs) has been predicted to have a very high thermal conductivity of over 2000 W m\(^{-1}\)K\(^{-1}\) at room temperature by first-principles calculations, rendering it a close competitor for diamond which holds the highest thermal conductivity among bulk materials. Experimental demonstration, however, has proved extremely challenging, especially in the preparation of large high quality single crystals. Although BAs crystals have been previously grown by chemical vapor transport (CVT), the growth process relies on spontaneous nucleation and results in small crystals with multiple grains and various defects. Here, we report a controllable CVT synthesis of large single BAs crystals (400–600 \(\mu m\)) by using carefully selected tiny BAs single crystals as seeds. We have obtained BAs single crystals with a thermal conductivity of 351 ± 21 W m\(^{-1}\)K\(^{-1}\) at room temperature, which is almost twice as conductive as previously reported BAs crystals. Further improvement along this direction is very likely. Published by AIP Publishing. https://doi.org/10.1063/1.5004200

Overheating presents a major challenge in the modern electronics industry, which is characterized by ever-shrinking dimensions and increasing power density.1 High temperatures not only limit device performance but also greatly reduce reliability and lifetime. To effectively dissipate heat from an electronic chip into the ambient, packaging materials with sufficiently high thermal conductivities are indispensable. The quest for materials with ever-higher thermal conductivities has recently been boosted by surprising theoretical prediction of Lindsay et al. that zinc-blende boron arsenide (BAs) may be among the most thermally conductive materials.2–5 Specifically, first-principles computations on BAs single crystals predicted that at room temperature, natural BAs has a thermal conductivity of over 2000 W m\(^{-1}\)K\(^{-1}\), and the value goes beyond 3000 W m\(^{-1}\)K\(^{-1}\) for isotopically pure BAs. This makes BAs comparable to diamond (about 2000 W m\(^{-1}\)K\(^{-1}\))6 and nearly an order-of-magnitude more conductive than some of the best traditional heat conductors such as copper (≈400 W m\(^{-1}\)K\(^{-1}\))7 and aluminum nitride (≈300 W m\(^{-1}\)K\(^{-1}\)).8

Experimentally, however, only limited success has been reported, due to a range of challenges in the crystal growth of BAs.9–12 It is well known that boron compounds are hard to make in dense bulk form. Growth of single crystals is especially difficult, yet is necessary for eliminating phonon scattering caused by grain boundaries and ultimately obtaining the predicted high thermal conductivity of BAs. Besides, arsenide synthesis is challenging because of the high toxicity and volatility of As. In addition, zinc-blende BAs decomposes into subarsenide \(\text{B}_{12}\text{As}_{2}\) at around 920°C, which is far below the melting point of B (~2027°C).13 This substantially limits the growth of BAs crystals using conventional crystal growth routes such as flux recrystallization and zone melting.3 Even though the synthesis of pure zinc-blende BAs single crystals has long been sought after, it remains a great challenge to obtain BAs single crystals of macroscopic dimensions and experimentally demonstrate the predicted ultrahigh thermal conductivity. BAs crystals with dimensions up to ~200 \(\mu m\) have been recently grown, and the thermal conductivity is measured to be only ~200 W m\(^{-1}\)K\(^{-1}\) at room temperature.9 Further, rod-shaped BAs crystals with a diameter of around 1.15 \(\mu m\) have also been fabricated and characterized with a thermal conductivity of ~186 W m\(^{-1}\)K\(^{-1}\).11 Compared to the theoretically predicted values, the measured thermal conductivities of BAs crystals are lower by about an order of magnitude, possibly due to As deficiency, anti-site defects, voids, impurities, twin boundaries, grain boundaries, and so on.

During chemical vapor transport (CVT) growth of BAs, gaseous B-related species are first transferred from the hot end of a quartz tube to the cold end and subsequently form BAs crystals by reacting with \(\text{As}_4\) vapor at the cold end. The supersaturation of the crystal component vapors drives the crystal growth and is controlled by the temperature difference between the source material and the crystallization front. It is worthwhile to note that defects can be easily introduced into the crystals during the growth process due to competitions between various near-energy-equivalent

---

(a)Author to whom correspondence should be addressed: zren@uh.edu
crystallization pathways.\textsuperscript{14} In order to grow crystals of large size and high quality, it is critical to properly manage the nucleation process and growth rate in the CVT process. Unfortunately, the spontaneous nucleation caused by supersaturation is normally uncontrollable. Tiny defects inside the quartz tube usually act as heterogeneous nucleation centers that initiate crystal growth. Due to the existence of these randomly distributed nucleation centers, the grown crystals are often found clustered, twisted, and tilted against each other. The structural quality of one crystal suffers from surrounding crystals since they limit space and induce stress. As a result, irregular morphology and micro-cracks are often present in typical CVT-grown BAs crystals. A possible solution to these issues is to use small BAs single crystals as seeds to better control the nucleation process and facilitate the growth of BAs single crystals with a larger size and higher quality. Note that unless the seeding is done properly (e.g., selection of BAs single crystals with a larger size and higher quality), one may not be realized.\textsuperscript{15}

Here, we report the synthesis of larger-size and higher quality BAs single crystals via placing tiny BAs single crystal seeds in an improved CVT system using pure B as the source material instead of traditional polycrystalline BAs precursors.\textsuperscript{9,10,12} First, pure As (Alfa Aesar, 99.999\%) and isotopically enriched B (Alfa Aesar, 99.9\%, >96\%\textsuperscript{11} B) with an As:B molar ratio of 1.2:1 together with some iodine (I\textsubscript{2}, Alfa Aesar, 99.999\%, \approx 50 mg per cm\textsuperscript{3} tube volume) were sealed in a fused quartz tube under vacuum. Subsequently, the quartz tube was placed in a horizontal two-zone furnace. The mixture of the source materials was placed at the high temperature zone which was held at \approx 890\degree C to avoid decomposition of BAs. Over the course of approximately two weeks, many aggregated BAs crystals with typical sizes of 200–400\,\mu m were found in the low temperature zone which was held at \approx 800\degree C. These crystals were crushed into pieces. Several small (\textlessthan 20\,\mu m), regularly shaped, and (111)-oriented single crystals were then carefully selected and placed at the crystal growth end of another quartz tube as seed crystals, as illustrated in Fig. 1. By repeating the growth process, we obtained some larger single crystals with much better morphology and cleaner surface thanks to seeded nucleation as compared to spontaneous nucleation. We found that excess As also forms As crystals at the cold end. Consequently, after the growth process, the crystals were collected and etched sequentially with concentrated nitric acid (70.0\%) and \textit{aqua regia} to remove all deposits on the surface of the BAs crystals. Finally, the crystals were cleaned with ethanol and de-ionized water for further characterizations.

The crystals grown without seeds were normally 200–400\,\mu m in size and of relatively poor quality with cracks, irregular facets, and multiple domains as shown in Fig. 2(a). By contrast, crystals grown from the seeds were bigger with a typical size of 400–600\,\mu m, much better morphology, and cleaner surface [Figs. 2(b) and 2(c)]. Spontaneously grown crystals with a much smaller size (20–200\,\mu m) were also found inside the quartz tube where no seeds were placed. X-ray diffraction analysis (Rigaku D-max IIIB X-Ray Diffractometer with a Cu K\textsubscript{α} radiation source) was performed on the crystals for structural characterization (Fig. 3). The shiny flat surface with light grey metallic luster of the as-grown crystals was found to be the (111) facet, the same as the seed crystals, thus confirming the effectiveness of the seeding technique for controlling nucleation and the direction of crystal growth. The rocking curve measurement of the (111) plane showed a full width at half maximum (FWHM) of \approx 0.056\degree, indicating relatively low crystal imperfection and high quality of as-grown crystals.

In addition to proper seeding, optimization of the source material and understanding of the detailed chemical reactions are also key to the growth of high quality BAs crystals. Chu \textit{et al.} claimed that using BAs powder as the source material would lead to faster CVT crystal growth than using pure B as the source.\textsuperscript{16} More recently, Lv \textit{et al.} also reported that a well-prepared polycrystalline BAs precursor was a proper source material.\textsuperscript{9} Both of them tend to suggest that the mechanism underlying the CVT process is

\textbf{Hot end : }\text{BAs(s) + 3I\textsubscript{2}(g) = Bl\textsubscript{3}(g) + AsI\textsubscript{3}(g),}
\textbf{Cold end : }4Bl\textsubscript{3}(g) + As\textsubscript{4}(g) = 4BAs(s) + 6I\textsubscript{2}(g).

In our effort to improve the crystal quality, we have systematically experimented with pure B, polycrystalline BAs powder with high As deficiency, and near-perfect (low As deficiency) polycrystalline BAs powder as the source material for CVT BAs crystal growth. We were able to collect BAs crystals at the growth end with either pure B or high As deficiency BAs precursor as the source material, but no BAs crystals were found when the BAs precursor with low As deficiency was used. Although no experimental data for the Gibbs free energy of BAs are currently available, one may draw the conclusion that at around 900\degree C, I\textsubscript{2} can hardly react with near-perfect BAs. In light of this observation, we propose below a more probable chemical mechanism underlying the CVT growth of BAs

\textbf{Hot end : }2B (s) + 3I\textsubscript{2}(g) = 2Bl\textsubscript{3}(g),
\textbf{Cold end : }4Bl\textsubscript{3}(g) + As\textsubscript{4}(g) = 4BAs(s) + 6I\textsubscript{2}(g).

The thermal conductivity of our sub-millimeter sized BAs crystals was measured using a noncontact optical pump-probe technique called time-domain thermoreflectance (TDTR).\textsuperscript{16,17} Briefly, one heats up an aluminum-coated BAs crystal using a high-power ultrashort (100 fs) pulsed pump
laser and monitors the subsequent cooling process with a
low-power probe pulse (100 fs, Fig. 4). The aluminum coat-
ing serves as both a laser absorber and a reflectance-based
thermometer. The measured cooling curve is fitted to a
Fourier heat conduction model to get the sample thermal
conductivity. The pump power is usually modulated to
increase the signal-to-noise ratio. This generates a complex
thermoreflectance signal which is recorded using a lock-in
amplifier. On the crystal shown in Fig. 2(c), thermal
conductivities in the range of about $80 \text{ W m}^{-1}\text{K}^{-1}$ to over
$300 \text{ W m}^{-1}\text{K}^{-1}$ were measured at different locations (see
supplementary material, Table S1). Meanwhile, we observed
variations in the surface conditions and Raman spectra
across the sample, which might have contributed to large
variations in the measured thermal conductivity. As an
example, Figs. 4(a) and 4(b) present the measured and fitted
thermoreflectance curves (the ratio between the real and the
imaginary part, or equivalently, the phase of the complex
signal) at a select spot, which yields a thermal conductivity
as high as $351 \pm 21 \text{ W m}^{-1}\text{K}^{-1}$ (Table S2, supplementary
material). In comparison, we note that the highest thermal
conductivities of the crystals shown in Figs. 2(a) and 2(b)
were measured to be $55.9 \pm 0.3 \text{ W m}^{-1}\text{K}^{-1}$ [see Fig. 4(c)]
and $131 \pm 13 \text{ W m}^{-1}\text{K}^{-1}$, respectively. The interface ther-
mal conductance between the aluminum coating and the
BAs crystal [Fig. 2(c)] was simultaneously fitted to be
$81 \pm 8 \text{ MW m}^{-2}\text{K}^{-1}$, indicating good interface quality.
Changing the fitted thermal conductivity by 20% resulted in
a large discrepancy between the computed and measured
data, suggesting good experimental sensitivity. The fitted
material properties lead to excellent agreement between
computed and measured thermoreflectance signals in both
the phase and the amplitude (see supplementary material,
Fig. S1), further confirming the experimental reliability.
Additionally, the electrical conductivity was measured to be
about $164 \text{ S/m}$ using the four-probe method, and the electron
thermal conductivity as estimated by the Wiedemann-Franz
relationship was on the order of $1 \text{ mW m}^{-1}\text{K}^{-1}$. Although
the measured thermal conductivity is an order-of-magnitude
lower than the theoretical predictions for single crystal BAs,
this value is higher than any of the previously reported val-
ues for single crystal BAs and comparable to the highest
thermal conductivities from traditional heat conductors.

The large discrepancy between the measured and pre-
pdicted thermal conductivities, combined with the relatively
large variation of thermal conductivity across the same crys-
tal, suggests that despite the improved growth technique and
crystal quality, some defects may still exist, such as As defi-
ciency, impurities, voids, and grain boundaries. For example,
it was recently predicted that for BAs crystals to have a room
temperature thermal conductivity over $1000 \text{ W m}^{-1}\text{K}^{-1}$,
an As vacancy of less than $3 \times 10^{18} \text{ cm}^{-3}$ is required.18
However, it remains a non-trivial experimental challenge to
identify and quantify these possible defects, particularly due
to difficulties in detecting B atoms. Temperature-dependent
thermal conductivity measurements are currently being pur-
sued to help identify the scattering mechanisms. Considering
the fact that some small crystals with poor quality were still
found at locations without seeds during the seeded growth,
there is clearly room to improve the seeded CVT growth tech-
nique. As a result, we are in the process of further suppressing
spontaneous nucleation on the tube walls. In addition, efforts are being made to understand more thoroughly the thermodynamics of the growth process in order to better control it and to ultimately grow BAs single crystals of macroscopic size with significantly improved thermal conductivity. On the other hand, computations incorporating increasingly more detailed microscopic scattering processes (e.g., four-phonon scattering and electron-phonon scattering) are being pursued, which usually lead to lower calculated thermal conductivities and would potentially explain part of the discrepancy.

To summarize, compared with previous reports, BAs single crystals with a larger size (400–600 μm), better morphology, and higher quality were obtained by placing tiny BAs single crystals as seeds in an improved CVT system in this work. These higher quality single crystals indeed demonstrate a higher thermal conductivity of about 351 W m⁻¹ K⁻¹ at room temperature, which is about twice as high as previously reported experimental values for BAs crystals. The seeds played a key role in the growth process, especially for the crystal size and quality. Further improvement is very promising.

See supplementary material for more details on the thermal conductivity measurements.

This work was funded by the Office of Naval Research under a MURI Grant N00014-16-1-2436, U.S. Air Force Office of Scientific Research Grant FA9550-15-1-0236, the T. L. Temple Foundation, the John J. and Rebecca Moores Endowment, and the State of Texas through the Texas Center for Superconductivity at the University of Houston.