tion, the product selectivity is not total, and its completeness depends on the kinetic energy of the molecular beam. On Pt(211), the steps and terraces each show their own energy-dependent product branching, as shown in figure 2. At the lowest kinetic energies, only the steps are catalytically active, and the vast majority of reactions are C–H fission to form CH_2D. At progressively higher energies C–D fission on steps, C–H fission on terraces, and C–D fission on terraces also contribute. At the highest energies, the branching ratio of C–H to C–D fission, deduced from the areas under the spectroscopic peaks, approaches 3:1, the expected value for a nonselective reaction.

Figuring out what the results mean for the reaction mechanism will require an intense theoretical effort. The very fact that quantum states are important to the reaction outcome means that the dissociation can't be described by a simple model; rather, theoreticians must simulate the detailed quantum trajectories of the molecules striking the surface. The Lausanne experimenters are working with several theory groups to convert their results into more accurate reaction models, with the ultimate goal being a predictive understanding of surface reactions on complex catalysts. And to better mimic the complexity of industrial catalysts, they're extending their experiments to Pt(531), whose steps are zigzag shaped.

Johanna Miller

References

1. H. Chadwick et al., *J. Chem. Phys.* **148**, 014701 (2018).
2. A. Gutiérrez-González, F. F. Crim, R. D. Beck, *J. Chem. Phys.*, in press.
3. R. D. Beck et al., *Science* **302**, 98 (2003); R. R. Smith et al., *Science* **304**, 992 (2004).
4. D. R. Killelea et al., *Science* **319**, 790 (2008).

Semiconductor crystals achieve record thermal conductivity

The synthesis of low-defect boron arsenide crystals could reduce overheating in electronic devices.

When a laptop or cell phone heats up from overuse, it's not just uncomfortable for the user. That excess heat also damages the circuitry and reduces the device's performance, energy efficiency, and life span. As modern electronic components are made smaller, their resistance rises. Heat dissipation has become a critical technological challenge for next-generation items, including microprocessors and integrated circuits, LEDs, and high-powered RF products.

Materials with high thermal conductivity help dissipate heat and improve the performance and reliability of those devices. However, developing a passive cooling option that is both cost-effective and reliable has been difficult. With a thermal conductivity of 2000 W/m·K, diamond is the best-known material for cooling. But it is expensive, has slow synthesis rates, and is of varying quality. Integrating diamond with silicon and other industrial semiconductors is also challenging because those materials have different thermal expansion coefficients.

Among metals, copper has the highest thermal conductivity at room temperature, 400 W/m·K, and is commonly used in industry for dissipating heat in electronics. Among binary compounds, silicon carbide, at 350 W/m·K, is favored for thermal management in personal electronics. To control the high-density heat generated in small, power-hungry devices, however, the ideal material would have a thermal conductivity at least as high as diamond's.

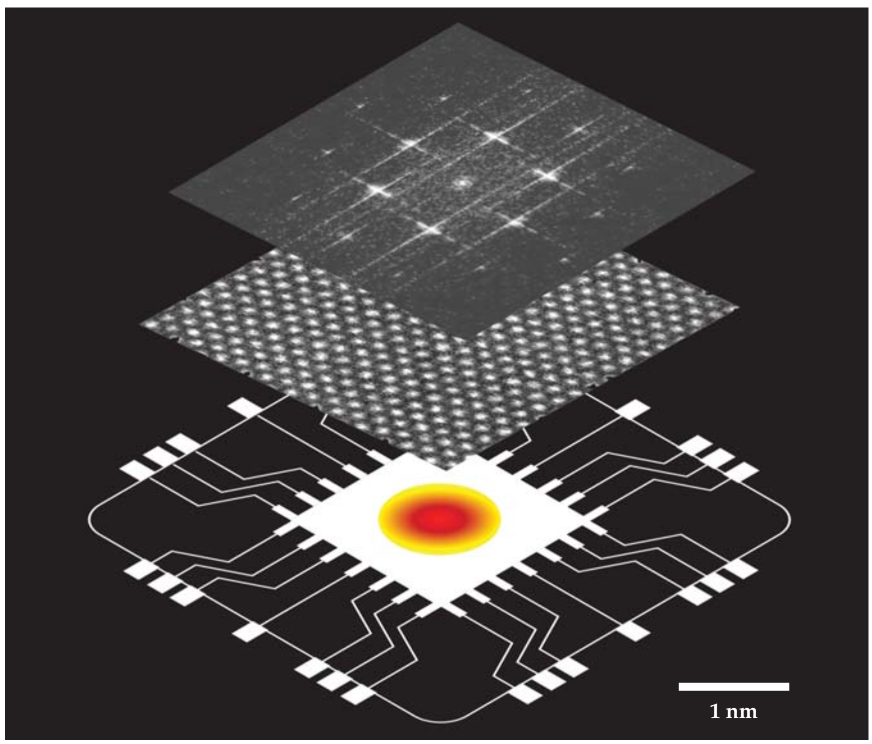


FIGURE 1. CONCEPT OF THERMAL MANAGEMENT AND A BORON ARSENIDE CRYSTAL. This illustration shows a computer chip with a hot spot at the center (bottom). A high thermal conductivity material like BAs could help dissipate the chip's heat. A transmission electron microscope image shows the atomically resolved lattices of a BAs crystal grown by UCLA researchers (middle). The electron diffraction pattern of the BAs crystal gives rise to clear bright spots, whose symmetry indicates the periodic structure and lack of defects in the crystal (top). (Image courtesy of Yongjie Hu.)

Now three research groups have synthesized boron arsenide (BAs) crystals that have a thermal conductivity of more than 1000 W/m·K at room temperature, exceeding that of all other materials except diamond.[1–3] BAs still has a long way to go in terms of size, consistency, and cost before it could be used in an actual device. Nonetheless, the new research vindicates theoretical predictions that have not been verified until now and might lead to the discovery of new practical materials. Figure 1 shows a conception of how a BAs layer could be inserted into a computer chip to help with cooling.

Good vibrations, in theory

In copper and other metals, nearly all heat conduction occurs via charge carriers. In diamond and similar nonmetals, which have no mobile electrons, heat is carried by phonons, or vibrations in the crystal lattice. When phonons scatter off each other, they slow down. A crystal structure with low phonon scattering has little thermal resistance and thus high conductivity.

In the early 1970s, Glen Slack of General Electric established with experiments and theory that high thermal conductivity in a nonmetallic solid required a simple crystal made of tightly bonded, lightweight elements, such as carbon.[4]

Theoretical predictions in 2013 by David Broido at Boston College and Lucas Lindsay and Thomas Reinecke at the US Naval Research Laboratory suggested that the conventional criteria for high thermal conductivity, as described by Slack, were incomplete.[5] High thermal conductivity could be possible not only in crystals comprised of lightweight elements but also in crystals with one heavy and one light atom. (See the article by Ilari Maasilta and Austin Minnich, PHYSICS TODAY, August 2014, page 27.)

In particular, the team's theory predicted that thermal conductivity in BAs could come close to that of diamond. The mass difference between boron and arsenic creates an energy gap between the two types of phonons, optical and acoustic, in the crystal. Optical phonons arise from out-of-phase vibrations between neighboring atoms, while acoustic phonons arise from in-phase vibrations. That large energy gap makes it harder for phonons to interact with each other. They can therefore travel efficiently through the crystals, resulting in greater thermal conductivity.

In 2017 Lindsay and Xiulin Ruan and his colleagues at Purdue University revised the 2013 theoretical results. The new work predicted that thermal conductivity of BAs should actually be close to 1300 W/m·K in defect-free crystals.[6] It accounted for scattering among combinations of up to four phonons, while the earlier work only considered combinations of three phonons. Although three-phonon combinations dominate scattering in crystals that have a small energy gap, they cannot occur across the large energy gap in BAs. Including a fourth phonon increases the number of possible combinations and is important to consider for determining the scattering in BAs.

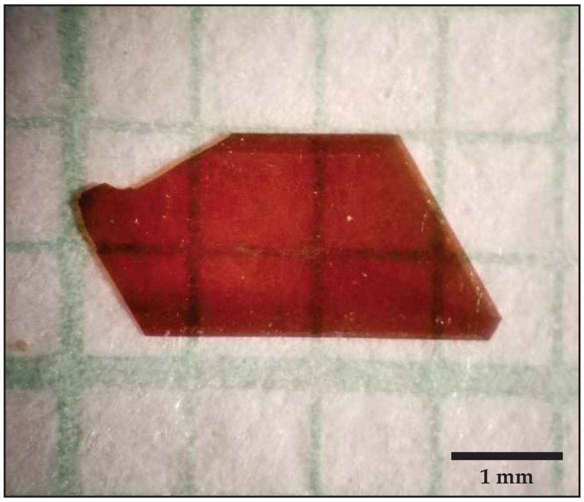


FIGURE 2. A 4 MM SINGLE BORON ARSENIDE CRYSTAL grown by researchers at the University of Houston. (Image courtesy of Zhifeng Ren.)

Almost defect-free

Synthesizing high-quality BAs crystals in bulk is difficult. Arsenic's high volatility tends to introduce defects and possible formation of unwanted atom combinations. Those defects and impurities dramatically reduce thermal conductivity by narrowing the energy gap between the phonons.

In 2015 Zhifeng Ren at the University of Houston and Bing Lv, then an assistant professor at the University of Houston, and colleagues synthesized BAs crystals using chemical vapor transport, a technique in which solids are vaporized and deposited as crystals. Unfortunately, despite the technique's promise, the crytals were riddled with defects. Yongjie Hu, then a postdoc at MIT, measured a thermal conductivity of only 190 W/m·K.

Now three teams led respectively by Ren, Lv, and Hu have each succeeded in optimizing the technique to synthesize crystals with thermal conductivity of at least 1000 W/m·K at room temperature.

The teams vaporized solid boron and arsenic in chambers that contained hot and cold temperature regions. Different nonreacting gaseous agents carried the two elements from the hot end to the cold, where the two combined to form crystals. Using a technique called time-domain thermoreflectance, each team measured the thermal conductivity on micrometer-scale regions of the surface.

Lv, now at the University of Texas at Dallas, and David Cahill of the University of Illinois at Urbana-Champaign measured room-temperature thermal conductivity of 0.5 mm crystals.[1] Repeated measurements on 50 samples, grown in different batches, revealed variations in thermal conductivity. The researchers used Raman spectroscopy, x-ray diffraction, and transmission electron microscopy to study the BAs samples for defects. They found a correlation between the thermal conductivity and the defect concentration, with the lowest-defect samples achieving the highest conductivity (1000 W/m·K).

Ren's team at the University of Houston grew larger crystals up to 4 mm in size (see figure 2). Gang Chen at MIT measured those crystals' local values of thermal conductivity[2] at 1000 W/m·K. By making additional thermal transport measurements on a larger scale, across more than 2 mm, Li Shi at the University of Texas at Austin concluded that the average thermal conductivity of the entire bulk crystal was also high, at 900 W/m·K. "Bulk measurements give confidence that the high thermal conductivity isn't just at the local region," says Ren.

Hu's team at UCLA developed very high-quality 2 mm crystals that had undetectable defects. They also recorded the highest thermal conductivity of the three groups, 1300 W/m·K, as predicted by theory.[3] Local measurements were consistent across the entire large crystal. Hu's group took several years to learn how to control the synthesis precisely enough to make samples approaching the defect-free limit. "Our study exemplifies the power of combining experiments and *ab initio* theory in new materials discovery," says Hu.

Lab to market

For BAs to be useful in electronic devices, the researchers still must find ways to make larger samples and more of them.

A semiconductor wafer inside a mobile phone, for example, needs to be several centimeters in scale. Scientists need to understand and control the types of defects present in the materials and to make the synthesis process more robust.

Besides high thermal conductivity, BAs has other desirable properties for thermal control, including chemical inertness and a coefficient of thermal expansion similar to that of silicon. Still, Cahill warns that "we have no idea if boron arsenide can be produced at a practical volume. Maybe eventually, but would it be cost-effective? We just don't know."

Shi adds, "It remains a grand challenge to understand the defect-formation mechanism." Now that scientists have a method for synthesizing nearly defect-free crystal, they can also introduce specific defects. Boundary and point defects could affect phonon transport and thermal conductivity in different ways. In that way, BAs offers the opportunity to study the origin of high thermal conductivity itself.

Rachel Berkowitz

References

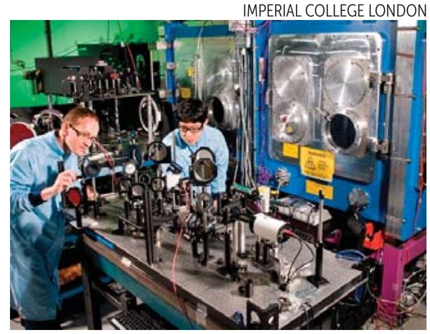
1. S. Li et al., *Science* **361**, 579 (2018).
2. F. Tian et al., *Science* **361**, 582 (2018).
3. J. S. Kang et al., *Science* **361**, 575 (2018).
4. G. A. Slack, *J. Phys. Chem. Solids* **34**, 321 (1973).
5. L. Lindsay, D. A. Broido, T. L. Reinecke, *Phys. Rev. Lett.* **111**, 025901 (2013).
6. T. Feng, L. Lindsay, X. Ruan, *Phys. Rev. B* **96**, 161201 (2017).

PHYSICS UPDATE

These items, with supplementary material, first appeared at www.physicstoday.org.

MAKING PIONS WITH LASERS

IMPERIAL COLLEGE LONDON



Of the 140 or so two-quark composites known as mesons, pions are the lightest. First discovered from tracks left by cosmic rays in photographic emulsions, pions are brought fleetingly to life whenever high-energy protons slam into other particles. Besides Earth's atmosphere, pions are also produced in particle accelerators, supernova explosions, and the interstellar medium. Now an international team led by Karl Krushelnick of the University of Michigan has demonstrated a new way to make pions: with short, intense pulses of laser light. The method depends on laser wakefield acceleration (LWFA). When a plasma is hit with a laser pulse, the electrons respond far faster than the sluggish, heavier ions do. As the pulse propagates, it is followed by a wake—a wave of charge separation—whose electric field gradient exceeds those in conventional accelerators by at least 1000 times. In their implementation of LWFA, Krushelnick and his collaborators used 43 fs pulses from the 300 TW Astra Gemini laser at the UK's Rutherford Appleton Laboratory (the photo shows the experiment at the facility). A pion-producing shot begins when laser pulses are fired into a cell containing helium gas. The resulting ionization and wakefield acceleration generate a beam of 1 GeV electrons, which passes through a 1.5-cm-thick lead target to produce additional electrons, positrons, and gamma rays. Electrons and positrons are removed from the beam by magnets. The surviving gammas hit the final target, a 20-cm-long rod of aluminum. When a gamma encounters an ^{27}Al nucleus, it yields either ^{26}Al and a neutron or, at higher energies, ^{27}Mg and a positive pion. Positive pions last just 26 ns before they decay into an antimuon and a muon neutrino. The researchers inferred the particles' presence by recording the 843 keV gammas, which the unstable ^{27}Mg nuclei emit when they decay. With the help of the FLUKA simulation code, the team estimated that each shot generated 150 ± 50 pions. (W. Schumaker et al., *New J. Phys.* **20**, 073008, 2018.) —CD

ARAGONITE CRYSTALS GROW IN TIGHT SPACES

Calcium carbonate's two common forms, calcite and aragonite, are widely found in nature—most notably, in the shells of mollusks and sea snails. Aragonite's abundance is puzzling, though. Despite being only slightly less stable than calcite, aragonite almost never crystallizes from solution in ambient conditions. Researchers seeking the secret to aragonite biomineralization have examined several possibilities—the presence of proteins, scaffold molecules, and organic additives, for instance—all of which can influence nucleation processes. Fiona Meldrum and her colleagues at the University of Leeds in the UK have now shown that the secret may be much simpler: confinement. They found that aragonite crystallizes inside submicron-diameter pores of arbitrary depth without any special additives and in amounts that depend only on the diameter of the pore.

The finding emerged from dozens of experiments using pores created by accelerating heavy ions and shooting them through polycarbonate films. In different-sized pores the researchers precipitated calcium carbonate by mixing two aqueous solutions—one made of calcium chloride and magnesium chloride, the other made of sodium carbonate and sodium sulfate. Analyzing the precipitates with x-ray diffraction and Raman spectroscopy revealed a trend with pore size: As the diameter was reduced from 1200 nm to 25 nm, the percentage of aragonite increased while that of calcite decreased. Whereas the largest pores contained almost entirely calcite, reactions in the smallest ones produced nothing but aragonite rods, as pictured here, even in the absence of magnesium or sulfate ions. The researchers speculate that the effect is attributable to the local ionic environment of the confining, curved surface. A slightly negative charge at the pore membrane produces an inhomogeneous ion distribution near the pore's center, which is thought to promote the nucleation of aragonite. The effect may also be tunable. A linear relationship exists between the weight percentage of aragonite and the inverse of the pore diameter. (M. Zeng et al., *Proc. Natl. Acad. Sci. USA* **115**, 7670, 2018.) —RMW PT