COVER

The World's Best Gallium Nitride

A little Polish company you've never heard of is beating the tech titans in a key technology of the 21st century

BY RICHARD STEVENSON // JULY 2010

Photos: Robert Laska

Gallium dust: [Left] Ammono’s first gallium nitride crystals were tiny, and metallic impurities gave them a brownish tint.

Gallium Jewel: [Right] After nearly two decades of refinement, Ammono’s growth technique now yields wondrously fine hexagonal crystals up to 2 inches across.

Want to revolutionize the electronics industry, become a multimillionaire, and earn your place as an immortal in the tech pantheon? Your job is simple: Figure out a cost-effective way to make really good, reasonably large crystals of pure gallium nitride.

With such crystals as the foundation for the growth of devices made of the same material, manufacturers would have a far richer yield of the violet lasers on which the optoelectronics industry increasingly depends. For example, the short wavelengths of these lasers are needed to read the hyperfine, data-rich line that rings the discs in Blu-ray players and in the latest game machines. Better gallium nitride would also let automakers make the power-handling circuitry in their hybrid electric vehicles more efficient, improving mileage and possibly even affordability. And with a fabulously good crystal foundation, LEDs could perform better, speeding the demise of the century-old incandescent bulb.

So far, though, gallium nitride crystals of good size and archangelic purity have been beyond the grasp of all but one of the companies that have worked for years to create them. That company’s based not in Japan, Korea, or even the United States, but in Poland. Meet Ammono, the greatest success story in materials science you’ve never heard of.

The company got where it is today by bucking the common wisdom in the industry. Instead of growing crystals with vapor deposition, the approach that all the leading gallium nitride substrate manufacturers take, it grows them the way the Earth does: under high heat and pressure.

Ammono, in Warsaw, is building up its stock of superhigh-quality gallium nitride crystals measuring 2 inches (51 millimeters) at their longest dimension. In a year or so it expects to have enough to start slicing some of them, salami-style, to produce wafers that can be turned into the round substrates on which semiconductors are grown. Admittedly, 51 mm is puny—a sixth the diameter of standard silicon wafers. But this size dominates today’s market for gallium nitride substrates, which are used as the foundation for making violet lasers. Analysts’ estimates of the market vary wildly, but everybody agrees it’s upward of US $100 million and that its double-digit rate of growth won’t end anytime soon.

It gets better: If Ammono increases the crystal size to 100 mm or more, major players in the silicon industry should start knocking on the company’s door, hoping to exploit other advantages of gallium nitride besides the color of the light it emits. For instance, it conducts heat far better than silicon does. By making large substrates from gallium nitride rather than from silicon, you can provide a better foundation for the diodes and transistors that convert battery power into a form that a hybrid electric car can use. That’s because the high currents heat up the chip, and if it’s made of silicon, it’ll need a water-cooling system of its own. Chips made of gallium nitride can simply share the cooling system of the internal-combustion engine, cutting costs and increasing the energy efficiency of the car. This potential market will grow along with sales of hybrid electric vehicles; according to analyst Philippe Roussel from the French firm Yole

Développement, chip production will gobble up 800 000 of these 100-mm substrates in 2015.

Photo: Robert Laska
Gemlike perfection: Robert Dwilinski, president of Ammono [with crystal], and cofounders Leszek Sierzputowski [left], Roman Doradzinski [right], and Jerzy Garcznski [far right].

That kind of success would fulfill a long-held ambition of Ammono's president, Robert Dwilinski, who pioneered the development of the firm's novel gallium nitride crystal growth process nearly two decades ago. The inspiration for its efforts can be traced back to a weekly seminar that Dwilinski attended as a physics undergraduate at the University of Warsaw. He vividly remembers a talk given by Izabella Grzegory, a researcher at the High Pressure Research Center of the Polish Academy of Sciences, also in Warsaw. She lauded the strengths of a family of nitrides that promised to enable production of LEDs with outputs ranging from the ultraviolet to the infrared. And she claimed that their performance would be stunning.

Unlocking the true potential of these devices required technological progress, including the development of a good substrate. Gallium nitride devices today are often built on substrates of sapphire, silicon carbide, or even plain silicon. But in each of those materials, the atoms in the crystalline lattice are spaced differently from those of gallium nitride, introducing a strain of the sort you'd get if you tried to stack goose eggs on top of a layer of chicken eggs. What you really want is a substrate sliced out of a large, pristine crystal of gallium nitride itself. In fact, such a foundation always gives the best results, and it is a prerequisite for laser manufacture.

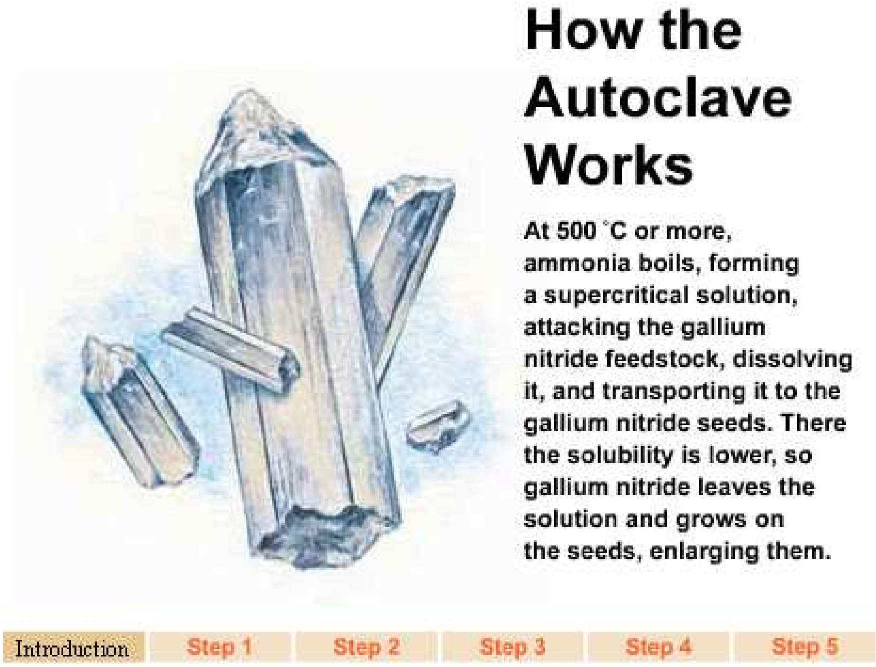
Dwilinski was intrigued by the challenge of making the first gallium nitride substrates, a quest that immediately became the central theme of his life. He resolved to pursue a Ph.D. in the subject, and to do that he needed a thesis advisor. Finding one wasn't easy, because Polish scientists tend to eschew commercially oriented research. Fortunately, one professor at the University of Warsaw did not: Maria Kaminska was willing to mentor him, and together they pursued several methods for growing gallium nitride crystals.

Most semiconductor substrates today are manufactured by a process invented in 1916 by the Polish scientist Jan Czochralski. You begin with a tiny, high-quality crystal to seed the growth process, then you rotate that seed crystal inside a melt of the same material. As you slowly pull out the seed, the molten material cools and solidifies around it, creating a cylinder that is tapered at the ends. That cylinder is called a boule, and it is what technicians slice to make wafers. The trouble is that gallium nitride won't succumb to the Czochralski process below a temperature of 2225 ℃ and a pressure of 64 000 atmospheres (6.49 gigapascals), comparable to conditions very deep within the Earth's mantle. "It is almost impossible to build such a system," says Dwilinski.

So he looked at other methods, such as combining gallium-based solutions and high nitrogen pressures in small vessels, an approach that can form gallium nitride at a more manageable 1500 ℃. Such efforts were already under way in the group where Grzegory worked, and while working on his Ph.D., Dwilinski teamed up with her and her coworkers. But he soon realized that although the quality of the gallium nitride crystals was outstanding, their dimensions were never going to be big enough for the mass production of commercial devices. Even today, this superhigh-pressure technique can produce crystals no larger than 20 mm, and the logic of high-pressure manufacturing makes it demonically hard to scale up the process. The thickness of the walls of the pressure chamber must increase by the cube of the increase in the size of the inner chamber; on top of that, the assembly must stay strong as temperatures rise to 1500 ℃ or more.

So Dwilinski began investigating alternative growth processes. He sought help from two friends he'd known in school and in the Boy Scouts who were working on their own Ph.D.s. Leszek Sierzputowski was an expert in chemical processes, and Roman Doradzinski was a theorist skilled in thermodynamic calculations. Sierzputowski worked at Warsaw University of Technology, and he roped in a colleague, Jerzy Garcznski, who had expertise in the design of high-pressure growth systems.

All four of them were attracted by the efficiency, low temperatures, and reasonable pressures associated with the commercial process used to make quartz crystals, which in a single run can turn out 1200 kilograms of product, most of which is made into crystal oscillators of the sort used in inexpensive wristwatches. Could this tried-and-true process be adapted for gallium nitride? The group resolved to find out.



How the Autoclave Works

At 500 ˚C or more, ammonia boils, forming a supercritical solution, attacking the gallium nitride feedstock, dissolving it, and transporting it to the gallium nitride seeds. There the solubility is lower, so gallium nitride leaves the solution and grows on the seeds, enlarging them.

Illustrations: John Rice; Animation: Michael Spector

More than a century ago, industrialists began making quartz crystals by simply mimicking the way nature does it. Today’s quartz manufacture is based on the process they developed. It begins with an autoclave—a vessel capable of withstanding high pressures and temperatures—filled to the top with hundreds of quartz seed crystals. Underneath those seed crystals is the feedstock, silicon dioxide gravel extracted from Brazilian mines. To begin making a single large crystal, you first put some water into the chamber. Then you shut the autoclave and turn on the heat, boiling the water and driving up the pressure within the container. At about 400 ℃, the pressure hits several hundred atmospheres, and the water is now neither a gas nor a liquid but a supercritical fluid. Think of it as a dense gas that moves freely and very quickly.

This supercritical water dissolves the silicon dioxide and, driven by convection, transports the dissolved material to the upper, cooler part of the autoclave, where the quartz seeds sit. Here the supercritical solution cools, reducing the solubility of the dissolved silicon dioxide and forcing it out of solution. This precipitate adheres to each of the quartz crystals, acquiring their crystalline form and thus increasing their size. To speed up what would be a glacial pace of growth, chemists add either alkaline metal hydroxides, particularly sodium hydroxide, or salts, such as sodium carbonate. These materials introduce negative ions that lead to a series of reactions that ultimately increase the solubility of the feedstock, which in turn makes it easier for dissolved material to move out of solution and onto the crystals, speeding their growth.

To adapt the process for gallium nitride, Dwilinski and his colleagues made three alterations: First, they replaced the silicon dioxide feedstock with gallium nitride, relying on alkali metal amide mineralizers; second, they swapped water for ammonia; third, they upped the temperature to 550 °C and the pressure to 5000 atmospheres. The one thing that they couldn’t do, though, was prime the process with a handful of gallium nitride seeds, which do not occur in nature. They hoped that temperature variations within the autoclave would spur the formation of tiny crystals, which could serve as seeds later on.

It didn’t work, partly because oxygen gas leaked into the autoclave and contaminated the growth. Then a tip from Herbert Jacobs, a professor at the Technical University of Dortmund, Germany, set them on the right track. Jacobs, too, was growing rare-earth nitrides using ammonia and heat, and he helped the Polish workers devise an oxygen-proof autoclave.

With their new, leak-proof autoclave in hand, the researchers performed their first trial run in 1993. It didn’t work at first, but in a few months they were regularly opening their autoclave to find a grayish liquid inside. Filtering this revealed a pale yellow powder containing tiny gallium nitride crystals. Initially, these crystals were only a few micrometers in size—far too small to see individually with the naked eye—but that didn’t stop Dwilinski from rejoicing. He knew he was onto something, because when these crystals were zapped with a laser, they lit up, a phenomenon known as photoluminescence, which couldn’t have occurred if they’d had many impurities. Probing with an X-ray source showed that they also had the correct hexagonal crystal structure. In other words, the crystals were first-rate.

The team had no money, and there were no domestic venture capitalists to appeal to. So they decided to plead their case with the leading gallium nitride developers in the United States, Europe, and Asia. The bold move paid off: In the fall of 1999, Shuji Nakamura, then employed by Nichia Corp., the Japanese firm he was boldly pushing into nitride optoelectronics, flew in to see them and was impressed with what he saw. On the advice of Nakamura—the inventor of the gallium nitride laser—Nichia would fund a joint research project to develop ammonothermal gallium nitride growth, and in return it would take a stake in Ammono’s intellectual property, as well as access to the crystals that were made.

So Ammono was under way, with the four researchers cofounding the company and renting a room in Warsaw from the Industrial Chemistry Research Institute. However, just a few months later, they heard the news that shocked the entire nitride community: Nakamura was leaving Nichia for the University of California, Santa Barbara.

The Nichia-Ammono relationship survived Nakamura’s departure. Before he left, Ammono had already found a great ally in Nichia’s Yasuo Kanbara, an open-minded and enthusiastic researcher who had already been mulling over the idea of ammonothermal growth of gallium nitride. He started visiting Ammono for a week every few months, a schedule he kept for several years. He also helped by sending Ammono’s materials back to Japan, where researchers characterized and tested it.

Ammono’s first challenge was to improve the design of their autoclaves, which tended to produce a lot of tiny gallium nitride crystals but also allowed them to dissolve slowly back again into the ammonia solution from whence they had come. To avoid a "two steps forward, one step back" process, in 2000 Ammono developed a new autoclave that more precisely controlled the temperature profile in the internal chamber. By optimizing the difference in temperature between the various parts of the autoclave, the researchers could make the most out of a peculiarity of the interaction of gallium, ammonia, and the alkali metals. Generally, a warm solvent can dissolve more material than a cool one, which is why hot tea dissolves sugar more easily than iced tea. But if you put gallium in ammonia, with the addition of small amounts of alkali metals, you get what’s called retrograde solubility instead: The solubility decreases with increasing temperature.

This peculiarity has a major impact on autoclave design. Here’s how: The high-temperature, seed-containing zone must be placed physically below rather than above the low-temperature zone containing the feedstock. That way, the ammonia solvent attacks the gallium nitride feedstock at the top of the autoclave, first dissolving it and then transporting it to the higher-temperature seed crystals below. There, where the temperature is higher, the solubility is lower, and gallium nitride precipitates from solution and grows on the seed.

What this means is that the seed can be hotter than the feedstock. At this high temperature the atoms are more mobile and therefore more likely to take up the correct position in the lattice, rather than getting stuck in the wrong place and marring the crystal. Another advantage of this arrangement is that unwanted impurities in the crystal are kept to a minimum, because they are actually less soluble at the lower temperatures prevailing in the upper part of the reactor. There they are forced out of solution and onto the surface of the autoclave.


Photo: Robert Laska

Ammono’s Autoclaves: In a single run, they now produce over 70 2-inch crystals of gallium nitride.

Dwilinski’s next step was to scale up the crystals. He started by taking crystals produced in one growth run and putting them back as seeds in the next. But when the crystals reached a certain size, the autoclave constrained them from getting any bigger. So for the past 10 years Ammono has built a succession of ever-larger autoclaves.

At some point between 2000 and 2003—the company refuses to say exactly when—it was able to make its first 1-inch-diameter gallium nitride substrate. Many other companies would have crowed about it in public, but Ammono kept quiet, sharing the philosophy of its Japanese backer. "People know that if Nichia announces something, it's not just an idea," says Dwilinski. "They achieve something, develop it to production, have ready product, and then advertise this achievement together with something to sell."

Ammono kept striving to make bigger crystals. At some point, the autoclaves became so large that the company needed larger rooms to accommodate them. (Autoclaves are long and thin; the largest ones are about 3 meters high, and you may need another 3 meters of free space above that to take them apart for reloading.) In 2003, Nichia agreed to finance a move to more spacious quarters in return for shipments of substrates. Ammono found a plot 25 km north of Warsaw and built a two-story complex of offices, manufacturing facilities, tools to polish substrates and characterize them, and even a couple of guest rooms.

Today, with 50 people on its payroll, Ammono is still a tiny player in a minuscule niche of the semiconductor industry. But it makes what are widely regarded as the world's best gallium nitride substrates, at sizes of 25 mm and 38 mm. They're not big enough to use in commercial production, but companies still want them to investigate what's possible with the best gallium nitride available today.

Ammono is now trying to accumulate enough 2-inch seeds to begin manufacturing 2-inch substrates, the minimum size for laser manufacturing lines. Only substrates of that size and of surpassing quality—known as laser grade—will do. The company must also convince its customers that its material is significantly better and cheaper than what they are using today. The target is clear: A single 2-inch laser-grade crystal now sells for $5000.

Dwilinski says that Ammono's 2-inch material will be priced competitively, but he insists that the cost will fall as production ramps up, economies of scale kick in, and the manufacturing technology matures. He figures that the industry wants to pay $1000 for a 2-inch piece of gallium nitride, and here's the good part: He reckons that the target is within the reach of his ammonothermal growth method but impossible with the industry's standard method. Dwilinski says there's no reason why his costs shouldn't fall, in the long run, to those common for gallium arsenide: $200 for a 4-inch substrate, according to the global consulting firm Strategy Analytics.

The incumbent technology for manufacturing gallium nitride substrates is called hydride vapor phase epitaxy (HVPE). First, you heat a substrate, typically gallium arsenide or sapphire, to around 1100 °C, after which you waft a mixture of gaseous compounds containing nitrogen and gallium onto its surface. Here they decompose to release gallium and nitrogen atoms, which form a gallium nitride film that can be peeled off and sliced into substrates.

One of the strengths of HVPE is its fast growth rate, but with speed comes a higher rate of defects. "There is talk of crystalline growth at 800 micrometers per hour," Dwilinski says, "but people involved say that you need to work in the range of 50 to 100 µm per hour to avoid highly textured surfaces." (That is, you must avoid any unwanted deviation from the ideal, which is a surface that's flat on the atomic scale.) This rate is still about 10 times as fast as what you get in ammonothermal growth, but the total amount of product you can get through the factory isn't necessarily higher, because the autoclaves can be filled with hundreds of seeds at a time. In comparison, the formation of a gallium nitride crystal by HVPE tends to involve growth on one substrate at a time. What's more, ammonothermal growth can outperform HVPE on other fronts: Autoclave maintenance is simple because it doesn't need cleaning, and all the gallium is converted into product, versus less than 15 percent for HVPE.

Ammonothermal also trumps HVPE in material quality. Differences between the atomic spacing of the gallium nitride crystal and the substrate on which it's grown cause HVPE-grown gallium nitride to bend. Ammono's process, however, can achieve a substrate that's 100 times as flat as HVPE-grown material and has two or three orders of magnitude fewer defects, a mere 5000 per square centimeter. These defects are a major pain for laser manufacturers because they quench luminescence and shorten device lifetime.

Recent advances with gallium nitride lasers also strengthen Ammono's position. Over the last few years, researchers all over the world have been trying to extend nitride laser emission to the green part of the spectrum [see "Lasers Get the Green Light," *IEEE Spectrum*, March 2010]. One of the most promising ways to do so is by growing lasers on different planes of the gallium nitride crystal, known as the semipolar and nonpolar planes, which Ammono's superflat crystals can yield with particular ease. That's because the crystals' greater flatness allows them to grow, defect-free, to greater thickness—and that thickness is needed to exploit the nonpolar and semipolar planes.

Ammono's long-term commercial success hinges not only on offering the market a better product for today but also on fending off threats from nascent technologies. One of these, known as the sodium-flux method, has many admirers, including Dwilinski himself, but he still doesn't think it can match ammonothermal's growth. This seed-based rival process involves molten gallium, which is mixed with sodium to increase the amount of nitrogen that can be dissolved in this solution at typical pressures of 70 to 80 atmospheres. Two-inch crystals have been produced by this technique, and they do have a lower defect density than HVPE-grown seeds. However, variations in the ratio of gallium to nitrogen in the solution make it hard to grow many crystals in a given run.

Ammono has finally stepped out of stealth mode and started to court publicity. Technical conference presentations began in 2007, when the company caused a stir by appearing to come out of nowhere and claiming to have produced large, very-high-quality crystals. This came as quite a shock to delegates, who were used to hearing about a new idea at one conference, followed by reports of incremental progress over the next few years. But most of the nitride community now accepts that the company's material is very good.

One question hanging over Ammono is whether its superior substrates lead to superior devices. Nichia clearly knows the answer, but the notoriously secretive company isn't giving anything away. However, Dwilinski maintains that the answer is a resounding yes and that the substantial device benefits will soon become evident. Ammono is collaborating with some research institutions that fabricate devices, and the results generated by this effort should be published in the academic press later this year.

The company plans to begin shipping 2-inch substrates in the second half of next year. It also expects to produce its first 1-inch semipolar and nonpolar material, which will provide a great foundation for making blue and green lasers. Ammono expects to introduce 3-inch gallium nitride substrates in 2013 and 4-inch substrates in 2015.

Let's hope that this fascinating little Polish company finds a backer or two to speed the introduction of big substrates. Of course, it would be good news for the makers of game players, laser TVs, and hybrid electric cars. More important, it would be a triumph for the little guy who beats the world by thinking in new ways.

About the Author
Richard Stevenson got to hold a 2-inch (51-millimeter) crystal of gallium nitride "worth as much as a BMW sports sedan" while touring the Warsaw factory of its maker, Ammono. The little company makes these jewels better than just about anyone else, which is why the manufacturers of blue lasers are beating a path to its door. Stevenson, based in Wales, studied compound semiconductors for his Ph.D. at the University of Cambridge. His previous *IEEE Spectrum* feature, "Lasers Get the Green Light," appeared in the March 2010 issue.