

OutPost on the Endless Frontier[©]

EPRI e-News on Recent Key Developments in Energy Science and Technology
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Why Diamonds are a Girl's Best Friend

Everyone, at least everyone of my generation, remembers the lyrics sung by Marilyn Monroe in her inimitable breathless fashion paying homage to that rare form of carbon as a women's most precious asset in a male-dominated world. In today's (hopefully) more gender-neutral society, such sentiments sound dated. Diamonds are either an item of investment, like any other valuable commodity, or adornment independent of the sex of the owner. Even your correspondent wears one (on his right hand!).

What has any of this to do with possible future energy technologies?

To help you better understand, let me relate an incident from my physics PhD candidacy exam. As you may know already, these exams are a major rite of passage whose successful transit allows one to enter the sanctum sanctorum of your university's laboratories and libraries for the purpose of carrying out your doctoral thesis research. You also get to have a personal faculty advisor whom you may actually talk to occasionally.

The "prelims" can take either written or oral form, or both. In my case I attended a mid-sized eastern Massachusetts university notorious for its excessive arrogance and terrible football team where the graduate curriculum was considered the most rigorous in the universe and passing each course exam exceeded in difficulty any possible comprehensive test (no, it wasn't MIT!). Instead you underwent an extended, several hour, oral examination on the basic physical principles underlying one's proposed specialization, in my case condensed matter physics (solid state). Preparation for this ordeal, truly a defining moment in one's life, took several months of intensive study. I leave it to the reader to imagine the physical and mental state of the student as the make-or-break event of his future career approached.

After a few initial pleasantries about who I was and what I hoped to become, my first question, put by a professor well-known for fundamental work in laser physics and who would receive the Nobel Prize some 24 months later, was, "Tell me, Mr. Grant, why are diamonds a girl's best friend?"

More or less the following dialog ensued:

Grant: "Well, sir, they're valuable and they sparkle."

Professor: "That's interesting. Why is that?"

G: "Hmm...let's see...well, the sp^3 hybridization that leads to tetrahedral bond formation is fundamentally unstable for principal quantum number two and the index of refraction of tetrahedrally bonded carbon is the highest known for any transparent material within the visible spectrum."

P: "Gee, that's even more interesting. Are the two properties related in any way?"

G: "OK, there are several polytypes of solid carbon whose ground state energies are lower than that of the diamond sp^3 bonding, like graphite and these forms predominate, and that's why the former structure is rare. Since the O_h symmetry of the diamond form has a higher ground-energy than the larger quantum number intermetallics, the optical gap between filled and unfilled orbitals, and thus the optical polarizability and index of refraction, determined by second order k-dot-p perturbation theory, are both very high."

You get the drift by now. What has this old "war story" have to do with the future of electric power? All right...modern control of power flow and quality, such as high voltage dc transmission and flexible ac transmission and distribution systems (FACTS), indeed power conditioning devices of all types, depend on semiconductors with crystal structures and chemistry close to that of diamond. In this issue of *OutPost* we will focus on the materials science of present and future semiconductor platforms for power devices rather than on the devices themselves (this topic will be the subject of an upcoming *InSights* article).

As in a few past *OutPosts*, I need to ask that you bear with me through as painless as possible review of some necessary background physics -- here the science of semiconductors. I'll try to make it as much fun as I can (don't forget to read the footnotes - there are some "gems" to be mined there!). However, you may want to take a deep breath or a break right at this point...and at the other italicized subheadings as well!

A Quick Trip Through the Periodic Table

It turns out that many of the elements in the middle columns of the Periodic Table bond the same way as the diamond form of carbon...silicon for example. Forgotten the arrangement of the Periodic Table? Go grab a copy somewhere. I'll wait.¹

OK, you're back. Note the "Group IV" column, a downward sequence of carbon, silicon, germanium and tin (upward in atomic, or principal quantum, number). Because, as we go up, the outer bonding electrons are further away from the nucleus, they are more easily stripped away or combine with their nearest neighbors. This attribute leads to a lowering of the aforementioned "optical gap" or more precisely, "band gap," narrows. It goes from about 3.5 electron-volts for diamond, to about 1.5 for silicon, 0.7 for germanium and zero for tin. Because the spectral sensitivity of our eyes begins at about 2 eV (red), diamond is transparent, and Si, Ge and Sn all look shiny. However, if you were a honey bee, whose vision extends into the infrared to about 1 eV, a silicon crystal would look much more brilliant than diamond. Honey bees would save a lot of money on engagement rings.

There is another consequence, an extremely important one for power as it will turn out, is

that as you go up in the Periodic Table, the same ease of “stripping off” electrons goes hand in hand with bond strength between atoms. This reflects itself in lower temperature operation for germanium over silicon, and silicon over carbon in diamond form, with the same for breakdown voltage. Take germanium compared to silicon as an example: its bandgap is lower, thus a lower voltage is required for an electron to jump the gap, and, once free, more easily able to accelerate to energies that will break the weaker atom-atom bond strength and destroy the material. Same story for silicon compared to diamond.

The next section may give you more than you need to know to get the final point of this current *OutPost*, but I recommend continuing if you are interested in exactly how semiconductors work. Those readers wanting to “get on with it” should just skip to the section titled “*Good Neighbor Policy of the Periodic Table*” so don’t put away your chart yet.

How Semiconductors Semiconduct

The mysterious “sp³ hybridization” I brought forth during my candidacy exam, first formulated by Linus Pauling, Nobel Laureate in chemistry and peace and notorious for his advocacy of overdosing on vitamin C, is crucial to the physics and uses of semiconductors. Think of it as blending two types of electron waves, one (s) as sort of a fuzzy sphere and the other (p) as a set of three two-bladed propellers situated on the corners of a cube with the blades pointing along the cube edges. The mixing, or “hybridization” of these four waves results in a new single wave one can picture as sitting at the center of a tetrahedron with its lobes reaching out to its four corners. It’s sort of like being at the heart of the Great Pyramid of Cheops at Giza with five tunnels placed so you can see out to its apex and the four base corners, except that our “pyramid” is a tetrahedron with a triangular base, not a square one. Next envision arranging an array of C, Si, Ge or Sn atoms at the center of individual tetrahedrons such that the “tunnels” of each nearest neighbor align. The resulting “diamond” crystal structure is a periodic lattice of cubes with an atom on each corner, at the center of each square face, and four more one-quarter of the distance along the length of two of the three body diagonals of the cube - two interpenetrating face centered cubic lattices, if you will..

If you have difficulty following all this, never mind - it all works out. Trust me.²

We can push the tunnel analogy even further. Think of the tunnels (more formally, the “covalent bond”) between each atom as in fact two tunnels in parallel, one chock-full of all the electrons it can take (the “valence band”), and the other completely empty (the “conduction band”). Neither tunnel can sustain an electrical current since, in one case, the valence band or tunnel is full and no more electrons can fit in, and in the conduction band, there are no electrons available to carry current at all. Thus diamond, silicon and germanium are insulators (tin is a special case - buy me a beer at some future RAC or advisory council meeting and I’ll tell you why). Actually, though, they conduct slightly. This is because at any temperature above absolute zero, an electron in the otherwise full valence tunnel will “boil over,” or hop, into the empty conduction tunnel and both will conduct a small electric current³ hence the name “semiconductor.” Light of the proper

wavelength and energy will do the same thing. The energy, either thermal or optical, required to “jump from tunnel to tunnel” is simply the bandgap referred to earlier.

There is one further aspect of a semiconductor that is vital to application. Back to the tunnel analog. Think of the electrons and holes³ as a fluid - then the wider the tunnel, the more easily the current flows, i.e., higher electrical conductivity, more usually referred to by the more intrinsic term “carrier mobility,” the conductivity divided by the number of electrons or holes in the respective tunnels. Our “tunnel width” is determined by the principal quantum number of the electron waves combined in the sp^3 bonds, thus carriers in silicon are more mobile than diamond, and germanium more than silicon.⁴

Good Neighbor Policy of the Periodic Table..

Have a look the elements on each side of Group IV, the Group III and V elements, gallium and arsenic astride germanium, aluminum and phosphorus - silicon, boron and nitrogen - carbon. It turns out that if we combine boron with nitrogen we get BN in which the Bs and Ns occupy the same atomic positions as C in diamond, with many of the same physical properties as diamond. We can also “cross” III-V elements to make compounds like GaN, and even alloy Group IV elements to form SiC, silicon carbide, for example, all of which behave in general like the Group IV elemental semiconductors. Just like the elemental semiconductors, C, Si and Ge, the bandgaps of these compound semiconductors depend on their atomic weight, or equivalently, their principal quantum number, i.e., the lighter the elements, the wider the bandgap. Thus materials like SiC, GaN and diamond itself became known as “wide bandgap semiconductors (WBGs)” as measured relative to silicon.

The Moral of Semiconductor Materials Science: “Ya gotta clean up your act before ya get down and dirty.”⁵

There is another extremely important role the III-V elements play in the practical application of semiconductors. The chef’s adage that, “it’s the pinch of salt that makes the soup,” has its counterpart for semiconductors. Chemically pure semiconductors are essentially useless. Recall that they are basically insulators. Now phosphorus is chemically extremely close to silicon in that its s and p electrons undergo sp^3 hybridization when substituted for the former - with one critical difference - the sp^3 waves of phosphorus contain a spare electron which escapes easily into the conduction band tunnel permitting current to flow. Similarly, the sp^3 waves of aluminum lack one electron compared to silicon, so that P traps electrons out of the valence band tunnel thus creating a positive charge, or hole, that can also transport electricity. Chemical “doping” of germanium and silicon gives rise to terms you frequently hear connected to semiconductors, such as “donors (electron sources),” “acceptors (electron traps)” that yield adjectives like “n-type (negative charge carriers)” and “p-type (positive charge carriers)” as descriptors. The ability to tailor the electrical properties of semiconductors in this way led to the early (1940s) replacement of vacuum tube diodes by p-n junction germanium devices. If you pass current “backward” or “reversed” through a p-n junction, the flow of electricity will be blocked up to a certain high voltage, typically a

few thousand volts, above which “breakdown” occurs and the p-n junction is destroyed. If you change the direction of current flow to the “forward” or “on state” direction, large amounts (several hundred amperes) will flow above a certain “forward” or “turn-on” voltage, usually a few volts in magnitude. These three quantities, the reverse breakdown voltage, the on-state current and voltage drop, characterize the most important aspects of a semiconductor power device. Later on (1940s - 50s), the invention of the germanium junction transistor invented by Shockley, Bardeen and Brittain⁶ became the basis of the switchable power devices typified by the thyristor and its derivatives.

Silicon Rules

Silicon became the “semiconductor of choice” over germanium for almost all electronic applications by the middle 1970s, including high power. Why? Well, for five reasons mostly.

1. Its larger bandgap rendered it more robust in high power dissipation, higher temperature applications - not only in computers, but for power as well (a premonition of opportunities for WBGs).
2. It was as amenable as germanium to growth of large, pure single crystals (maybe even more so -- today the standard “boule” diameter range about six to eight inches, and in the lab, I’ve heard of 16-inches in meter lengths). Highly perfect silicon films can also be grown by a wide variety of vacuum and vapor deposition techniques. The lack of viable single crystal growth techniques presents a major barrier to the use of several of the WBGs.
3. It was just as chemically “dopable” as germanium (as we shall see, more difficult to do for some of the WBGs) and thus amenable for junction, or “bipolar,” device fabrication.
4. It was lighter than germanium (remember JFK’s committing the nation to a Man-on-the-Moon by 1969? Use of silicon lessened the payload burden considerably).
5. Finally, silicon oxidizes to several stable states compared to Ge which really has none. This was crucial to the development of the field-effect-transistor (FET), the workhorse of all computer technology today⁷. Quite ironically, FET devices are reasonably easy to fabricate with WBGs, but it is the old-fashioned junction transistor that we need to control power flow.

The huge push given silicon, especially in its preparation and purification, by the computer and communications industry trickled down by the 1980s to our business, resulting in thyristors and a multitude of other junction transistor embodiments⁸ that could replace old-fashioned gas-discharge thyratrons traditionally employed in high voltage dc inversion/rectification applications. Most significantly, these silicon switches enabled the Flexible AC Transmission System (FACTS) concept pioneered at EPRI.⁹

Beyond Silicon for Power Applications - Prospect For Wide Bandgap Semiconductors

So why isn't silicon good enough for our purposes? The answer is that it probably can suffice for the next five to ten years at least. Progress has been remarkable, and thyristor devices now exist in the laboratory that can stand-off 8000 volts, and transport 2000 amperes when on with a forward voltage drop slightly less than a volt.¹⁰ A variety of other silicon devices¹¹ have also been developed that, unlike thyristors, have "full cycle" turn-on, turn-off capability. Then what's the problem?

With silicon it's mostly the breakdown voltage and operating temperature that go along with its place among the Group IV elements, as we pointed out earlier. Silicon devices are approaching their physical limitations in that regard. Both properties are ultimately bounded by its bandgap of around 1.5 eV to approximately 10,000 volts and 200 C. To put this in perspective, imagine we want to "invert" a 500,000 volt bipolar, 2000 ampere high voltage dc power to ac. We would need at least 50 thyristors in series (today the number is in the several hundreds), each dissipating in the "on state" around 2 kW assuming a forward drop of one volt per device. That's a lot of individual elements that have to have closely matched properties and a lot of heat to draw off to keep them operating below 200 C.

Hence the need to have a long-range look at wider bandgap replacements for silicon. The three most promising material platforms, are, in order of most probable to most challenging, SiC, GaN and diamond. All three have a major barrier to overcome - there is a long way to go before any of them approach silicon in both crystalline perfection and microscopic purity - and the most important of the two is crystalline perfection.

Go back and have a look at a phrase I used in my oral exam: "...the sp^3 hybridization that leads to tetrahedral bond formation is fundamentally unstable for principal quantum number two..." As you surmised previously, this is physics-speak for why diamonds are rare. What I left unsaid before is that there is a small energy difference between bare "s" and "p" electrons that gets larger the lighter the element. This means it gets harder to "mix," "blend" or "hybridize" the s and p electron waves to get them to combine in sp^3 fashion and bond tetrahedrally with their neighbors. The almost universal tendency for light Group IV elements and III-V compounds is to form a wide variety of cubic (diamond-like) and hexagonal based structures, some quite exotic. The practical consequences are that it becomes extremely difficult to produce single crystals without a large number of defects arising from the near-equilibrium of other nearest-neighbor atomic arrangements called "polytypes".

One more very important point - forward voltage drop. Even if we approach the materials perfection attained in silicon for the WBGs, there remains an essential downside. The forward voltage drop of a switchable junction device depends on a number of factors, but one of them is the bandgap. Thus the main feature that makes WBGs attractive (high breakdown voltage) is a detractor with respect to turn-on. Let's consider a wide bandgap device with forward voltage drop of 5 volts for a given on-

current equivalent to a silicon unit. Say that silicon equivalent has a forward drop of 1 volt and a reverse breakdown at 10,000 volts. To keep the total forward power dissipated constant in our 500,000 HVDC example and reduce part count would require our WBG device to sustain a reverse bias of 50,000 volts (it is estimated 25,000 volts might be achieved in a hypothetical diamond thyristor). Clearly, reducing forward voltage drop will be a major goal for all WBGs junctions.

We'll finish off by reviewing briefly the current materials state of affairs in the three most promising WBG candidates under consideration to replace silicon. As mentioned earlier, actual devices will be addressed in a future *InSights*.

Silicon Carbide

Silicon carbide has been around a long time as a useful material technology, at least a hundred years. We know it commonly under its trade name, carborundum, a popular abrasive. However, for such application, SiC need be nowhere as pure as necessary for electronic operation. SiC in ceramic form is also a widely used refractory material for extremely high temperature (~ 1800 C) environments like heat shields for the space shuttle...and therein lies one of the central difficulties in forming single crystals of SiC preparatory to doping it and preparing it for electronic device application...you have to react its precursors, high purity powders of C and Si, at even higher temperatures, around 2500 C, in ultrahigh purity argon gas. The resulting vapor deposits on a single crystal seed which then proceeds to grow to about one centimeter thick. One of the tricks of the trade is to keep the temperature uniform across the surface of the growing crystal (some think within one or two degrees C, no mean feat in a background around 2500 C).¹²

It turns out that SiC can form in over 20 different crystal structures or polytypes; quite a mess.¹³ Several of these are cubic, or diamond-like, but the one which has greatest promise for device development (slightly larger bandgap and carrier mobility, somewhat easier crystal growth) is a hexagonal form designated "4H." However, 4H-SiC is plagued by a pernicious defect, a "screw" dislocation that results in a tube in the direction of crystal growth about 20,000 SiC units wide and millimeters long, a huge distance on an atomic scale, which was dubbed a "micropipe" (maybe it should have been called a "mini-manhole"). This defect is a killer for power applications, since under high voltage, a discharge occurs very much like that of a miniature lightning storm. At present, the best that can be achieved in 4H-SiC is about one micropipe per square centimeter. Nonetheless, this is good enough to make small prototype devices since one can "slice and dice" around these discrete defects. Another, much smaller, but much more prevalent, and perhaps one with more serious consequences, screw dislocation defect is currently under study to determine its behavior under high voltage conditions.

SiC can be readily doped to produce the kind of p-n junction with aluminum (p) and nitrogen (n) necessary to fabricate power devices and several junction diodes and thyristors have been investigated recently.¹³ The performance of current devices can be summarized in both blocking voltage and on-state power dissipation at about 10% that of the best silicon units. But, we're just getting started.

The principal drivers for silicon carbide (and additionally gallium nitride) material and device development are lower power metal-oxide-semiconductor field effect transistors (MOSFETs) and blue light emitting diodes (LEDs) for military application in highly stressed environments, such as high temperature and high frequency, high power radar.¹⁴ For this reason, EPRI has formed an alliance with the Department of Defense Advanced Research Projects Agency (DARPA) to co-sponsor materials and prototype device development with the expectation that improved performance p-n junction power devices suitable for future FACTS technologies will emerge as well.¹⁵

Gallium Nitride

At present, there are no known methods to fabricate crystals of GaN, whose structure comes in two flavors... "zincblende," close to the diamond atomic arrangement, and "wurzite," a hexagonal first cousin, by cooling from a melt (like we make ice, salt and silicon), or by direct mass transport (like SiC). Very excellent (better quality than SiC and approaching silicon in low defect density), but thin, crystalline films of GaN can be grown on sapphire¹⁶ by a method called metallo-organic chemical vapor deposition (MOCVD) which essentially means decomposing an organic complex of gallium in a vapor stream containing an acid (like nitric). GaN as grown is naturally n-type (excess nitrogen). It can be made p-type by (you guessed it) doping with a Group II element like magnesium. Very good MOSFETs and LEDs have been fabricated using GaN as the base semiconductor, in fact, GaN blue LEDs are now commercially available.¹⁷

In principle, p-n junction devices could be made perhaps suitable for FACTS-like application. The catch is the phrase, "but thin," just used to describe the resulting crystal thickness. To stand off reasonably high voltages, we need to have about 1 mm of semiconductor on each side of the p-n junction (high bandgaps help, but are not enough). If we had a GaN growth rate of 1 micron (millionth of a meter) per minute (very, very fast for GaN), it would take about 17 hours to achieve the necessary thickness - not a "showstopper," but definitely a challenge.

No one has yet made a GaN thyristor - to try this is one of the targets of the EPRI/DARPA Advanced Power Electronics Initiative.¹⁸ An unknown issue is the question of "minority carrier lifetime." What's that, you say? OK, the holes and electrons travelling in our dual interatomic tunnels want to "recombine." After all, they are oppositely charged and you know what that means. There are essentially two ways they can get together. One for the electron to "directly" jump from its tunnel to the hole with the energy of recombination or annihilation producing a photon, or light. The other is for the electron to knock around some surrounding atoms first, losing most of its energy to making heat, and then collapse exhausted on a hole - "indirect" recombination as it were. Charge carriers that recombine directly have short lifetimes compared to those that do it indirectly. Which way it goes depends on the details of the wiggles in the band structures shown in Ref. 4. Suffice it to say that the electrons and holes in semiconductors like GaAs and GaN do it directly by emitting light and that's why they're the lasers used by the CD player in your boom box.¹⁹ However, the holes travelling

through an n-type layer (thus the term “minority carrier”) in a thyristor have to live long enough to get to the other side to allow the device to “latch” or switch and do its job. Computer simulations of hypothetical GaN thyristors indicate that the minority carrier lifetime should be long enough - just. When we get one actually built, we’ll let you know if that’s really true.

Diamond

Carbon, the element comprising diamond, would prefer, thermodynamically, to solidify as graphite instead (remember my “exam” remarks?)²⁰. Graphite - pencil “lead” - is black and soft, the exact opposite of diamond. At one time, earlier this century, coal was thought to be a separate form of carbon, but close examination showed it to be mainly microscopic graphite. Graphite’s crystal structure is that of an elongated hexagonal cylinder with the carbon atoms along the cylindrical axis about two and a half times further apart, a result of a different blending of the carbon s and p electron waves, sp^2 instead of sp^3 . This stacked plate of hexagons slides or slips very easily, thus graphite has many applications as a dry lubricant.²¹ A third form of solid carbon was synthesized about ten years ago, a form long suspected from spectral observations of interstellar debris. This new form, its simplest structure in the shape of a soccer ball with a carbon atom at each intersection of stitches, 60 in all, was dubbed “fullerene” in honor of the famous “geodesic dome” architectural design of R. Buckminster Fuller. Since then, a fairly large number of derivative shapes have been discovered. One, for instance, is an oblate spheroid of 70 carbon atoms called footballene - what else? And next came carbon nanotubes...but all this is a subject for a future *OutPost*. Finally, there is a linear structure known called “carbene” which, at least to the knowledge of your correspondent, has never been synthesized in lengths more than 5 or 6 atoms long, and which we actually pursued for a while as a potential candidate for high temperature superconductivity.

The methods of choice for producing diamond fall into two categories. One - nature’s way - is to just squeeze as hard and hot as you can on graphite. This approach was pioneered at GE’s corporate research center in the 1950s and is the principal manufacturing method for diamond machine tools and abrasives today. Recently, remarkably large (about half a centimeter!) synthetic diamonds have been made using improved pressure cells.²² The second is the use of chemical vapor deposition methods similar to those employed for GaN. The raw material is simply methane, so let’s not burn it all yet. Great advances have been made in the last 20 years in the deposition of higher and higher quality diamond films.²³ The uses of diamond films for a variety of purposes, especially as thermal sinks, has increased greatly in the last five years.

On paper, diamond seems like the ideal semiconductor for power applications - on paper. But here, progress has been slow.²⁴ The main difficulty has been to get films of even marginal crystalline quality of the level required for electronic devices. In addition, there is only one widely accepted report of n-type doping of diamond. Diamond films have an inherently high concentration of hydrogen because they are made from methane. This excess hydrogen tends to “compensate,” that is, electrically neutralize, Group V “good

neighbors” like phosphorus, when it is introduced substitutionally for carbon. The one successful report of n-type doping yielded electron carrier concentrations too small for device purposes.

Recently, there has been much interest in an unusual property of diamond compared to any other semiconductor - its desire to want to “lose” electrons, a property known as “negative electron affinity.” In sufficiently high electric fields (units are volts per centimeter) such as those surrounding sharp points (recall Ben Franklin’s lightning rod), diamond will release a large number of electrons, in some instances approaching in density those found in old fashioned vacuum tubes, thus coining for the phenomenon the term “cold cathode emission.” In fact, if a “space charge” can be produced near such a cathode, a modern embodiment of the vacuum tube triode might be possible. Such an opportunity has not escaped the notice of the flat panel display technology community, and a number of companies and research institutes are actively exploring the fabrication of “diamond tip” arrays where the emission from tips a tenth of a millimeter apart could be individually used to illuminate an overlaid phosphorescent screen. One might consider using a similar array, with the tips all connected in parallel, as a high power switch. If we assume each individual tip can manage 100 microamperes of on-state current, then 10 million in parallel, all switching simultaneously, covering a 30 cm on edge square, conceivably would constitute a new power device. We will monitor developments on the use of diamond tip arrays for flat panel display application closely.

Time to “Switch Off”

By now you should see that there is more to diamond and its wide bandgap cousins than esthetics alone. Potentially higher operating temperatures, higher breakdown voltages, smaller footprint and part count...all offer significant leverage over the current silicon technology for FACTS devices. However, there are at least two significant challenges.

The first is to get our industry to use silicon for FACTS right now. It’s here and it works at a price quite reasonable compared to the total infrastructure required for a FACTS installation. There’s not much use in developing the next generation semiconductor technology if the current one is not being used to its full potential.

The other is to overcome a feature of the WBGs they share with the jewelry enterprise - high cost. The highest purity silicon wafers used in high power electronic “hockey pucks” today run around \$30 per wafer, a mere 3% of the cost of the finished device which averages \$1000 per unit.¹⁰ Right now, the best SiC wafers commercially available of the necessary diameter go for around \$2000. GaN could potentially be much cheaper (the sapphire substrate is likely to be the highest cost item) and has the best chance of achieving silicon-like quality. We will have to see if minority carrier lifetime is a problem. Of the three candidates, CVD diamond is by far the cheapest for raw manufacture, but it is problematic that it will be as processable as silicon for p-n junction device fabrication in the foreseeable future, and its use in field emission configuration may require such massive parallelization and associated close element tolerance as to be impractical to manufacture in sufficient quantity.

Oh, there's one final critical issue. Suppose diamond never does makes it as a practical FACTS device. Can you imagine the inimitable Marilyn crooning, "Gallium nitrides are a girl's best friend?" Uhh...naw, I didn't think so.

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¹If you don't have one handy and can get on-line, you can find a periodic table at <http://www.cs.ubc.ca/cgi-bin/nph-pertab/tab/periodic-table>

²Just in case you don't (trust me), here are three web sites offering good visualizations and an immense amount of background on semiconductor physics.
<http://cst-www.nrl.navy.mil/lattice/struk/a4.html>.
<http://ostc.physics.uiowa.edu/~wkchan/SOLIDSTATE/CRYSTAL/diamond.html>
<http://www.ai.mit.edu/people/tk/tks/diamond-structure.html>

³It's fairly clear why a few electrons in the conduction band would carry current, why the valence band conducts is a little more subtle - removing a few electrons from the valence band out of the many (10^{23} !) that are available actually produces an effective positive charge - a "hole" in the middle of a negative sea of electrons. Mind you, this is not a real positive electric charge. Interestingly, this can actually happen in the relativistic formulation of quantum mechanics. In the 1930s Paul Dirac predicted that real positive charge could be produced spontaneously from the vacuum, which he named "positrons," the first inkling there might exist "antimatter." His prediction was confirmed a few years in observations of radioactive decay and in experiments performed in the early particle accelerators. This is definitely probably more than you wanted to know.

⁴If you really want to see what the quantum mechanical nature of these valence and conduction band tunnels really look like, visit the following web pages. The roman and greek letters along the x-axis denote the direction and magnitude dependence of the electron and hole momentum in the tunnels. This arcane notation is known in my trade as "Boukhart-Smolukowski-Wigner space groups," which we joke we invented to terrify chemists so they would stay off our turf.

C (diamond): http://www.nirim.go.jp/~kobayak/Table/BAND/band_gif/c3360.ps.gif

Si: http://www.nirim.go.jp/~kobayak/Table/BAND/band_gif/si_lda_5125.ps.gif

Ge: http://www.nirim.go.jp/~kobayak/Table/BAND/band_gif/ge5200b.ps.gif

Sn: http://www.nirim.go.jp/~kobayak/Table/BAND/band_gif/sn60c.ps.gif

⁵Historical note: If you consult the materials handbooks of the 1920s and 30s, you'll find germanium and silicon classified as "metals." They were so impure their valence and conduction band tunnels contained extrinsically a huge number of holes and electrons, so much so, they behaved like metals! It was not until fundamental studies of their physical properties began at Bell Labs in the 1940s (as well as in fascist Germany), that their "act got cleaned up." Today silicon crystals can be made that have one defect or impurity for several trillion silicon atoms. This curtain has "yet to go up" completely on this performance for the wide bandgap semiconductors, which have orders of magnitude

improvement ahead to approach the current level of silicon purity.

⁶The three Bell Labs researchers were awarded the Nobel Prize in Physics for their discovery. This was just the first for John Bardeen, who later won a second for the explanation of superconductivity. For us physicists, this accomplishment is the equivalent of Joe DiMaggio's 56-game hitting streak...unlikely to be surpassed for centuries.

⁷Another historical note: The field effect transistor, the workhorse of all modern computers, was first conceived by Bell Labs in the 1920s. A great example of a great idea before its time. The "field effect," by which an electric field applied to a semiconductor across an insulating barrier (oxide) can control the flow of carriers (much like the grid immersed in the space charge region of a DeForest triode, an acquaintance which clearly dates your correspondent!) and produce amplification. The drawback is that, due to the small volume portion of the semiconductor the field effect controls, not much power can be handled. Practical realization of the FET had to await the arrival of photolithographic technology in the 1960s.

⁸A common feature of these devices is a single crystal of silicon doped with regions of n- and p-type impurities to control switching thresholds and current/voltage characteristics. For power applications of the HVDC variety, wafer platforms of the order 7-10 cm in diameter are required to handle high current levels and several millimeters thick to withstand high voltages. With packaging, their dimensions approximate that of a hockey puck, a term which has become their nickname. The need for reasonably thick substrates may make difficult the use of slow thin crystal film growth techniques which are the only method of fabrication for some WBGs, e.g., GaN. To see the specifications of current state-of-the-art silicon thyristors, visit: <http://www.siliconpower.com/products/C792.pdf> (You will need Adobe Acrobat Reader).

⁹N. G. Hingorani, IEEE Spectrum **30**, 40 (1993); N. G. Hingorani and K. E. Stahlkopf, Sci. Am. **269**, 78 (1993). Recent developments in FACTS will be the subject of an upcoming *OutPost*

¹⁰Silicon Power Corporation, private communication.

¹¹<http://www.siliconpower.com>.

¹²Both the United States and the former Soviet Union had rather extensive "dark side" programs in silicon carbide materials development. The military desire for high temperature robust semiconductors should be fairly obvious - ever spent much time inside a tank? In the early 1990s with the end of the Cold War, much of this previously classified work on SiC burst loose (the FSU had been slightly ahead of us) and the number of papers and conferences skyrocketed with a concomitant improvement in materials.

¹³Some good web sites to visit for the latest on SiC materials and devices are
<http://www.cree.com/products/sic/silicarb.htm>
<http://www.ecn.purdue.edu/WBG/>
<http://www.lerc.nasa.gov/WWW/SiC/facilities.html>.

¹⁴<http://www.darpa.mil/dso/darpa40/eto/p8.htm>

¹⁵<http://www.epri.com/news/releases/darpa.html>

¹⁶You might say sapphires were once the “next best friend” to diamond. Sapphire, aluminum oxide, and, when doped with a small amount of chromium, ruby, now can be made much more perfectly and cheaper by artificial methods than does nature.

¹⁷Coated with various phosphorescent materials, they make a very bright and efficient illumination technology compared to incandescent lamps. Most of the new traffic lights being installed in Japan use GaN LEDs.

¹⁸Visit the following web sites at the University of Florida and Cal Tech.
<http://www.mse.ufl.edu/Pearton/presentations.html>.
http://www.ssd.caltech.edu/ssdp/Group_Members/zzb/GaN_HighPower.html.

¹⁹Most semiconductors like Ge, Si, the majority of SiC polytypes, and diamond are “indirect,” so no problem making thyristor devices with them.

²⁰Eventually, all solid forms of carbon will evolve into graphite whose thermodynamic equilibrium energy is much lower than that of diamond. Fortunately, the kinetic barrier for the movement of carbon atoms from one form to the other is reasonably high, so that this process takes several eons at normal pressures and temperatures. You can thus tell your partner to rest easy - your symbol of commitment is for all practical purposes “forever.” On second thought, better to keep this bit of materials physics to yourself. You never know what might get him/her unnecessarily upset.

²¹Many, perhaps most, manufacturers of computer hard drives coat the surfaces of the disk platters with a very thin film of carbon. You want a slippery surface, so that when the read/write head hits it, which it does more times than you might realize, it sort of skips along like a stone thrown over water instead of auguring in and removing you from the payroll. On the other hand, for similar reasons you want the same film to be as impervious to impact as possible. The relative amounts of sp^2 and sp^3 hybridized carbon, and most critically, how to arrive at those values, is one of the most closely guarded secrets of the industry.

²²Your correspondent recently had in his hand just such a specimen, produced in the laboratory of Prof. Rajiv K. Singh at the University of Florida (rsing@mail.mse.ufl.edu). It was highly twinned (crystals within crystals) and very yellow due to the high content of atmospheric nitrogen, but impressive nonetheless. Incidentally, nitrogen is a common impurity in many natural diamonds. Such “yellow” diamonds come and go in fashion, and they are much cheaper than the clearer variety. If you get one for someone special,

keep this fact close. See Ref. 20.

²³An excellent, although somewhat dated, account of progress in diamond synthesis, can be found in the following article in Science, December, 1990:

<http://www.chem.wisc.edu/~newtrad/CurrRef/BDGTopic/BDGtext/dgpfms.html>

²⁴The September, 1998, issue of the MRS Bulletin, summarized both the materials and application situation for CVD diamond films. Be sure to click on the cover image.

<http://www.mrs.org/publications/bulletin/1998/sep/>

<http://www.mrs.org/publications/bulletin/1998/sep/>

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