

A different type of stable carbene, **8**, was prepared by Bertrand and co-workers (16). Here, the stabilization comes largely from donation of a pair of electrons from the phosphorus atom. Consequently, **8'** is a better description of this kind of compound (17). **8** retains typical singlet carbene reactivity, including stereospecific addition to olefins to form cyclopropanes.

Last year, Bertrand and co-workers reported the "push-pull" stabilized carbene **9** (18). The molecule is stabilized by electron donation from phosphorus (as in **8**). In addition, stabilization is derived from electron withdrawal by the electronegative CF₃ group. The molecule is stable in solution for several days at -30°C and shows singlet carbene reactivity, such as stereospecific addition to olefins to afford cyclopropanes **10** and insertion into the Si-H bond of Et₃SiH. The related carbene **11** is stable for weeks at room temperature. Its structure is similar to that of **8**, with a short P-C bond (1.544 Å) and a PCC angle of 162°. The carbene lone pair is delocalized into the electronegatively substituted aromatic ring, thus providing push-pull stabilization. Consequently, the C-C bond between the carbene center and the aromatic ring is also short (1.390 Å) (18).

The latest report from Bertrand and co-workers (1) describes the synthesis of stable (amino)(aryl)carbenes **12**. The species **12a** has a melting point of 16°C and an NCC angle of 121°, as expected for an ordinary singlet carbene; the C-C bond between the carbene center and the aromatic ring is essentially a single bond (1.453 Å). The N-C bond is 1.283 Å, shorter than in di(amino)carbenes. Thus, carbene **12a** exists essentially in the resonance structure **12'**. It retains the geometry of a typical singlet carbene, and its reactivity indicates typical carbene behavior. Unlike compound **11**, electron delocalization into the aromatic ring promoted by the electronegative CF₃ groups is apparently not crucial for stability: The (amino)(aryl)carbene **13** was stable in solution at -50°C for days and underwent C-H insertion into a *tert*-butyl group, typical of (aryl)carbenes.

This latest work by Bertrand and co-workers (1) shows that a single amine substituent, in combination with steric hindrance, can be sufficient to stabilize a singlet carbene that retains typical singlet carbene reactivity. It opens the way for a new wave of preparative chemistry of stable carbenes. Apart from the fundamental insight into the nature of divalent carbon compounds that can be expected to emanate from such work, sta-

ble carbenes are of much potential interest in catalysis. For example, di(amino)carbenes of type **6** have been shown to form exceptionally strong bonds with virtually all the transition elements and many lanthanides, and may thus surpass the ubiquitous phosphine ligands in organometallic catalytic chemistry.

References

1. S. Solé, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **292**, 1901 (2001).
2. M. Gomberg, *Chem. Rev.* **1**, 91 (1925).
3. J. B. Dumas, E. Peligot, *Ann. Chim. Phys.* **58**, 5, (1835).
4. J. U. Nef, *Liebigs Ann. Chem.* **287**, 359 (1895).
5. A. J. Arduengo III, *Chem. Unserer Zeit* **6**, 32 (1998).
6. W. v. E. Doering, A. K. Hoffmann, *J. Am. Chem. Soc.* **76**, 6162 (1954).
7. P. S. Skell, S. R. Sander, *J. Am. Chem. Soc.* **80**, 2024 (1958).
8. H. Tomioka, *Acc. Chem. Res.* **30**, 315 (1997).
9. K. Hirai and H. Tomioka, *J. Am. Chem. Soc.* **121**, 10213 (1999).
10. H. L. Woodcock *et al.*, *J. Am. Chem. Soc.* **123**, 4331 (2001).
11. A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **113**, 361 (1991).
12. W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **36**, 2163 (1997).
13. D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **100**, 39 (2000).
14. R. Breslow, *J. Am. Chem. Soc.* **80**, 3719 (1958).
15. R. Kluger, *Chem. Rev.* **87**, 863 (1987).
16. A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **110**, 6463 (1988).
17. T. Kato, H. Gornitzka, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **122**, 998 (2000).
18. C. Buron, H. Gornitzka, V. Romanenko, G. Bertrand, *Science* **288**, 834 (2000).

PERSPECTIVES: APPLIED PHYSICS

Toward Diamond Lasers

Phillip John

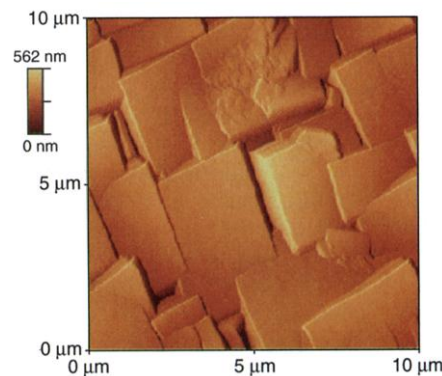
Most devices that emit light at ultraviolet and visible wavelengths, from visual displays to optical data storage, use II-VI and III-V binary materials, where the Roman numerals denote elements in the main groups II to V in the Periodic Table. The larger the band gaps of these insulating materials, the shorter the wavelength of the emitted light is. Shorter wavelengths are desirable because they potentially allow greater data storage, but suitable materials at these wavelengths are harder to find. Blue lasers were thus a much greater challenge than red or green ones until Akasaki (Meijo University) and Nakamura (Nichia Chemical Industries) developed a room-temperature blue laser based on GaN, which emits at wavelengths below 450 nm (1). Nichia now fabricates commercial quantities of blue lasers, and many groups worldwide are developing GaN light emitters and photodetectors with promising commercial prospects (1).

For light emission at even shorter wavelengths, diamond is a potentially promising material because of its large band gap (about 5.5 eV). Optimism for diamond electronics has, however, been tempered by the difficulty of synthesizing single-crystal diamond by chemical vapor deposition (CVD), necessary to achieve sufficiently high charge carrier mobility for electronic applications. New reports indicate that these problems may soon be overcome. On page 1899 of this issue, Koizumi *et al.* (2) report a diamond-on-diamond (homoepitaxial) pn junction made by CVD that emits at 235 nm. This report is an important milestone and complements similar reports by Tokyo Gas Company and Kobe Steel.

The electronic properties of CVD diamond films have been improved steadily over the last decade. The growth technologies have been refined, and concomitant progress has been made in doping methodologies, which are used to tune the electrical conductivity. For example, doping with phosphorus results in an extra electron available for conduction (n-type dopant),

whereas doping with boron results in conduction due to "holes" (p-type dopant).

Intrinsic (undoped) and boron-doped p-type materials are readily available through in situ doping during CVD growth or postgrowth ion implantation. Hole mobilities of around 50 to 100 cm² V⁻¹ s⁻¹ in randomly oriented polycrystalline films increase to about 280 cm² V⁻¹ s⁻¹ in highly oriented diamond films grown on silicon surfaces. The hole mobility of 300 cm² V⁻¹ s⁻¹ quoted by Koizumi *et al.* for their homoepitaxial junction is of the same order



Epitaxial diamond. This atomic force microscope image shows the typical faceting of epitaxial diamond films grown on silicon by CVD. As Koizumi *et al.* show, appropriately doped diamond-on-diamond films can form pn junctions emitting in the ultraviolet.

The author is in the Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK. E-mail: p.john@hw.ac.uk

as in these highly oriented diamond films grown on silicon. Such heteroepitaxial films exhibit columnar growth and have low defect densities in the grains and shallow-angle grain boundaries.

Further improvements of the electronic properties can be anticipated. For example, Kobe Steel has claimed hole mobilities of up to $1400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for homoepitaxial films. The use of substrates such as platinum may enable hole mobilities of natural single-crystal diamond (about 1800 to 2400 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) to be reached. Very recently, biased enhanced nucleation on iridium was reported by Schreck *et al.* (3). The latter two techniques appear to result in coalesced grain boundaries, which may be "transparent" to the transport of charge carriers.

In contrast to p-type dopants, the incorporation of phosphorus and other n-type dopants (with the aim of producing a shallow donor) into diamond has been inefficient. This has been the main impediment to diamond bipolar devices. The main approaches have been in situ doping or cold implantation of phosphorus ions followed by rapid thermal annealing. Koizumi *et al.* used gas-phase doping in the fabrication of both regions of their p-n junction. While a Ti/Au layer was used to make electrical contact to the p-type layer, a patterned ohmic contact to the n-type region was formed by Ar^+ implantation to form a matrix of graphitic dots. Implantation of rare gas atoms into the dia-

mond lattice yields n-type conductivity. The n-type behavior is, however, associated with the creation of defects in the band gap. This process must be minimized to avoid defect-induced conductivity, dopant compensation, or formation of dopant-vacancy complexes.

Okano *et al.* (4) first reported the production of n-type P-doped polycrystalline diamond films. They reported carrier mobilities of about $50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, slightly lower than the $60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported by Koizumi *et al.* In 1999, Sakaguchi and co-workers (5) announced shallow n-type doping using sulfur as a dopant. The results were initially difficult to replicate, but evidence for sulfur doping has now been reported by other groups. For example, Stutzman and co-workers report electron mobilities of $250 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 290 K (6). There is ample scope for further improvements in light-emitting CVD diamond p-n junctions.

Natural diamonds are diverse in their individual properties compared to CVD diamond. Notwithstanding the difficulties of processing bulk diamond, the presence of inclusions, impurities, and—most important—nonuniformly distributed nitrogen defects degrades the electronic properties. Semiconducting type IIb crystals containing boron are rare, and, in any event, the boron dopant is not homogeneously distributed and predominates along growth fronts.

Relatively small single crystals of diamond may be grown reproducibly at high

pressure and high temperature, but, until recently, contamination by the transition metal catalysts and by nitrogen complexes and aggregates was a problem in growing electronic-grade diamond by this route. The process has been improved by using nitrogen getters (materials used to remove impurities), but it is too early to predict whether high-pressure–high-temperature diamond will be used extensively in active electronics or whether the material is suitable for diamond light-emitting diodes.

To date, CVD is the most promising route to diamond films for use in diamond electronics, as demonstrated by the junction reported by Koizumi *et al.* (2). Predictions (1) of a market of \$1.3 billion for GaN-based optoelectronic and electronic devices within a few years may even be conservative. Ultraviolet diamond lasers have a similarly promising future. For example, key applications in DVD data storage will be enhanced with such a laser. Numerous other applications are envisaged.

References

1. Blue Lasers: Lighting Up New Markets in Displays, Optical Storage, Medical Devices, and More, Report D219 (Technical Insights, Frost & Sullivan, NY, November 2000).
2. S. Koizumi, K. Watanabe, M. Hasegawa, H. Kanda, *Science* **292**, 1899 (2001).
3. M. Schreck, F. Hörmann, H. Roll, J. K. N. Lindner, B. Stritzker, *Appl. Phys. Lett.* **78**, 192 (2001).
4. K. Okano *et al.*, *Appl. Phys. A* **51**, 344 (1990).
5. I. Sakaguchi *et al.*, *Phys. Rev. B* **60**, 2139 (1999).
6. M. Stutzman, personal communication.

PERSPECTIVES: GENOMICS

Are There Bugs in Our Genome?

Jan O. Andersson, W. Ford Doolittle, Camilla L. Nesbo

For evolutionary biologists working on the exchange of genes between species (lateral gene transfer), the most exciting news from the human genome sequencing project has been the claim by the "public effort" (1) that between 113 and 223 genes have been transferred from bacteria to humans (or to one of our vertebrate ancestors) over the course of evolution. We, and probably many others wanting to test whether this result is really solid (2), have been beaten to the punch by Salzberg and colleagues (3). Their analysis, appearing on page 1903 of this week's issue, suggests that the actual number of bac-

terial genes in our genome may be lower than the predicted 223. These authors argue that there are other biologically plausible explanations besides lateral gene transfer that could account for the presence of bacterial genes in our genome.

The claim for lateral gene transfer from bacteria into vertebrates (as exemplified by our own species' genome) was based on similarity searches. Such searches involve screening vertebrate genomes for sequences that are very similar to bacterial genes but are absent from other eukaryotic genomes. Genes shared by vertebrates and bacteria that are not found in other eukaryotes are considered to be probable bacteria-to-vertebrate transfers (BVTs). The 113 to 223 BVTs in question have significant similarity to bacterial sequences but no "comparable similarity" to genes in other completed eukaryotic genomes (1).

Salzberg *et al.* (3) now provide a careful reanalysis of these data (1) with a similar

but more conservative approach that includes the addition of data from Celera's version of the human genome (4). As in the original study (1), the investigators' goal was to detect possible transfer of genes by analyzing gene distribution across taxa. They found 135 genes in the public effort's data set of 31,780 protein-encoding sequences (Ensembl proteome) and 89 genes in the Celera proteome of 26,544 proteins that were possible BVTs (3). This is similar to the public effort's conservative estimate of 113 possible bacterial genes in the human genome (1). Lateral gene transfer is not the only factor that could explain these results. For instance, differential gene loss (that is, random independent loss of genes in different eukaryotic lineages) may yield similar gene distribution patterns. The Salzberg *et al.* reanalysis demonstrates that the calculation of the number of bacterial genes in the human genome is highly dependent on how many nonvertebrate genomes were screened against the human genome. These authors found a downward trend in the number of BVTs observed when the human genome was screened against an increasing number of nonvertebrate genomes. Such a pattern is indeed

Enhanced online at
www.sciencemag.org/cgi/content/full/292/5523/1848

The authors are at the Canadian Institute for Advanced Research, Department of Biochemistry and Molecular Biology, Dalhousie University, Halifax, Nova Scotia B3H 4H7, Canada. E-mail: joanders@is.dal.ca, ford@is.dal.ca, cnesbo@is.dal.ca