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Materials science

How to make macroscale non-crystalline diamonds

Alfonso San-Miguel

A diamond shatters easily, despite it being the hardest natural material. Atomically disordered forms of diamond made from buckyballs might not only overcome this problem, but also allow other properties to be optimized. **See p.599 & p.605**

The brilliant facets of diamonds have entranced people throughout history and are a result of the ordered atomic structure of these gemstones. But this order comes at a cost: it makes diamonds fragile. In contrast to quartz and many other crystalline materials that produce atomically disordered forms, a disordered — and potentially less fragile — form of diamond has not been available. In this issue, Shang *et al.*[1] (page 599) and Tang *et al.*[2] (page 605) report how to produce atomically disordered diamond-like materials with millimetre-scale dimensions, constituting a breakthrough for materials science.

Atomic-scale order can be a problem for materials scientists, as illustrated by the mineral quartz. Quartz is a bad choice of material for a car windscreen, because it is difficult to shape and easily broken by objects hitting it. Glass is a much better choice, because it can be conveniently engineered, is easier to shape and does not disintegrate so readily[3]. Yet quartz and glass are made of the same atoms, have the same chemical formula, and their architectures are built from the same tetrahedral SiO_4 subunits.

The crucial difference between glass and quartz is the atomic order: quartz is crystalline, which means that its atomic bonds follow a regular pattern throughout the material; whereas glass lacks any such order and is said to be amorphous. This difference contributes to the divergence of the mechanical properties of the two materials — the lack of long-range atomic-scale order in glass means that there are no planes of atoms that provide directions in which the material breaks easily. These 'cleavage planes' are the reason why crystalline gemstones can be cut by applying a blow in just the right direction. They also explain why diamond is fragile, despite it being the hardest naturally occurring material.

Diamond consists of tetrahedrally arranged carbon atoms, linked by covalent bonds. The physical properties of diamond strongly differ from those of graphite, which is another crystalline form of carbon. These differences derive from the organization of electrons — called electron hybridization — in the carbon bonds. In graphite, electrons organize in a way that allows each atom to form three bonds in a plane, thereby producing a 2D hexagonal lattice; this is called sp^2 hybridization. Graphite is made by stacking planes of sp^2-hybridized carbon atoms, and it has many disordered forms[4].

By contrast, the electrons in diamond exhibit sp^3 hybridization, which enables each carbon atom to form four bonds pointing in different directions from the atom's centre to the corners of a tetrahedron. Diamond therefore has a 3D architecture generated by the sp^3-hybridized carbon bonds, and no form of it was known that had long-range atomic disorder and could be produced as 3D macroscale samples. A type of sp^3-hybridized carbon known as diamond-like carbon comes close to having such disorder, but only films of this material have been produced, which incorporate varying amounts of hydrogen atoms[5]. Samples of materials proposed to be amorphous diamond have also been reported, but only in quantities similar to the size of dust particles[6,7].

The methods now reported by Shang *et al.* and Tang *et al.* for making millimetre-scale forms of disordered diamond are broadly similar to the original method used to make crystalline diamond: a carbon-based material, such as graphite[8] or carbon nanotubes[9], is subjected to high pressure and temperature in a large press. However, in contrast to previous work, both research groups used fullerite as a starting material, which consists of a crystalline arrangement of fullerenes — soccer-ball-shaped C_{60} molecules that are also known as buckyballs.

Moreover, the syntheses were carried out

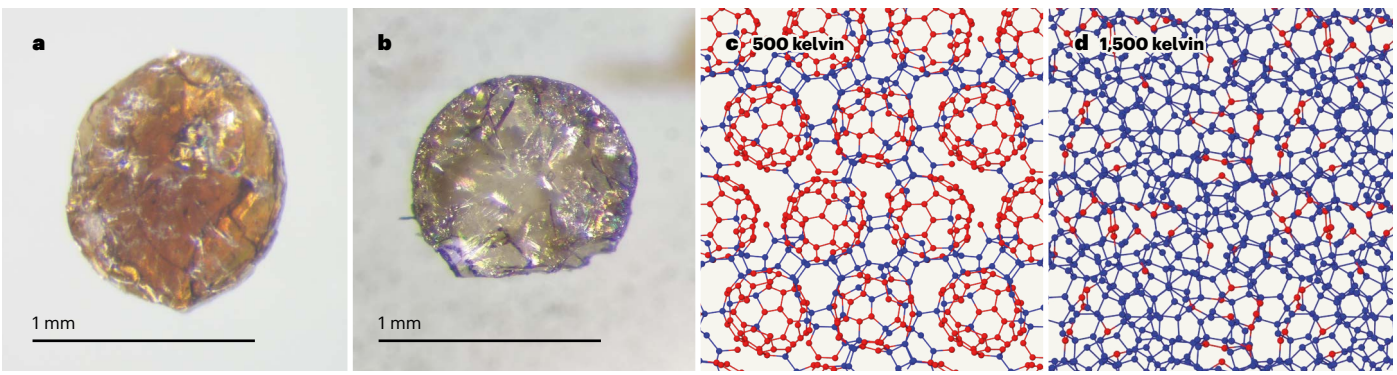

Figure 1 | Atomically disordered diamond forms from buckyballs. a, Shang *et al.*[1] subjected buckyballs to high temperatures and pressures, and produced amorphous diamond — a form of carbon that has the same type of chemical bonds (sp^3 bonds) as crystalline diamond, but that lacks atomic order. **b**, Tang *et al.*[2] used the same approach to make paracrystalline diamond, which can be thought of as a composite that consists of an amorphous carbon matrix containing nanometre-scale, severely distorted diamond crystals. **c**, **d**, Tang and colleagues' computer simulations show how the pressurized buckyballs (which contain sp^2 bonds, red) polymerize and then collapse to form a disordered structure that comprises mostly sp^3 bonds (blue) as the temperature increases.

in large-scale pressure cells at temperatures of about 900–1,300 °C, and the pressures were of the order of 27–30 gigapascals (1 GPa is 10^9 pascals). These pressures are much lower than were used in previous studies that reported dust-particle-sized amorphous diamond[6,7]. The fullerene molecules polymerized, collapsed and finally transformed into transparent materials that could be recovered at ambient conditions (Fig. 1a, b).

In both cases, the authors studied the hybridization and atomic arrangements of the carbon atoms in the obtained materials using various techniques, including X-ray diffraction, high-resolution electron microscopy and atomistic modelling (Fig. 1c, d). Both research groups report that their materials contain atomically disordered sp^3-hybridized carbon: bulk disordered diamonds have finally been made. However, although the analytical results might look similar at first sight, the structures of the obtained materials are not the same.

Shang *et al.* conclude that their material has a completely amorphous sp^3 diamond structure, whereas Tang *et al.* describe their material as an amorphous diamond paracrystal. A paracrystal is a material that exhibits medium-range order — the atoms are ordered over short distances (nanometre scales), but disordered over longer distances. Tang and colleagues' paracrystal can be thought of as a composite consisting of an amorphous carbon matrix filled with different percentages of nanometre-scale, severely distorted crystals (known as paracrystallites).

An interesting question is why fullerenes seem to have a central role in the formation of disordered diamond structures. Fullerene molecules contain 12 pentagons of carbon atoms, and a well-established principle of geometry is that there is no way to fill space to form a periodic (crystalline) structure using only pentagons. Therefore, the presence of a large number of pentagons in fullerites might make the formation of crystalline structures more difficult, as was observed in the present studies.

The two disordered sp^3-carbon materials have promising properties for applications. Both have exceptional mechanical properties. Furthermore, the paracrystalline material has excellent chemical stability and the amorphous material has outstanding thermal and optical properties. However, the high pressures needed to synthesize these materials limit the size of the samples that can be prepared to the millimetre range, and this presents a serious hurdle for the development of industrial-scale processes.

Nevertheless, the findings of the two studies not only extend our knowledge of atomic disorder in materials, but also add to our understanding of how to use such disorder to engineer physical properties. In particular, the discovery of diamond paracrystals might enable the development of new classes of carbon–carbon nanocomposites that have tunable thermal, electrical, optical or mechanical properties. Paracrystals could potentially take advantage of both the non-directional mechanical properties of the amorphous matrix and phenomena known as the Hall–Petch and inverse Hall–Petch effects[10,11], through which the mechanical properties of the materials could be improved by tuning the size of the paracrystallites.

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