Mater. Res. Soc. Symp. Proc. Vol. 956 © 2007 Materials Research Society 0956-J01-01

Thinking about Diamond

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ABSTRACT

Diamond is valued mainly as a symbol of power and value (the girl's best friend) and as a solution to many materials processing problems (the engineer's best friend). The 1950s saw both striking developments in diamond synthesis and the beginnings of the rise of silicon as the semiconductor of choice. Since then, silicon has transformed the world. Diamond has reinforced its known roles, and found niches that exploit its special qualities. It is also one of the carbon materials that, in combination, have a variety of superb properties. Could there be bigger opportunities for diamond, more than mere niches, arising from the major social needs: the life sciences, the information technologies, energy, and perhaps others. I attempt to identify areas that might develop formidably.

STATUS DIAMONDS AND WORKING DIAMONDS

Diamond has created legends and it has created industries. Its special properties have also spawned what can legitimately be called a wealth of niche applications. Here I ask the question: will we see more new *major* applications, ones that create new legends or transform an industry?

Today, there are just two ways in which diamond is unique and dominant: the status diamond, and the working diamond. Status diamonds are symbols of power. Their beauty, rarity and cost limits ownership. When Kings, Queens, Emperors and Presidents are crowned, it is diamond, more than rich gold and rubies, that hints most effectively at power and continuity of tradition. Even a model who wears a special stone for a few minutes feels pivileged by the transient sense of ownership. The status diamond will be expensively set and worn by the richest people. Working diamonds are entirely different. The stones and their mountings are chosen for economy and effectiveness. Even before the industrial revolution, Diderot's 1751 *Encyclopaedia* showed a tradition for diamonds as tools, with many diverse applications for these working diamonds. Even small and ugly diamonds have value.Their mechanical properties dominate, with significant niche applications such as thermal sinks.

The *major* applications for diamond thus exploit only a fraction of diamond's special properties: visual for status diamonds, and mechanical for working diamonds. Could there be other major applications, perhaps exploiting different diamond properties? The materials developments of the last 50 years include silicon becoming the semiconductor of choice, many new and better-developed polymers, and the transformation of communications by silica-based optical fibres. Diamond has been synthesised. Could it have new, major, radical opportunities?

Cambridge University Press
978-1-107-40880-7 - Diamond Electronics—Fundamentals to Applications: Symposium held November 27-30, 2006, Boston, Massachusetts, U.S.A.
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ON DIAMOND'S FUTURE

Diamond is already a very successful material, a source of power and an object of beauty. Its mechanical properties still win through because of diamond's impressive performance and diamond's track record that is tough for new materials, despite the claims of "superhard" alternatives. Diamond's wealth of materials properties better than those of any common material have led to many niche applications, though other materials remain dominant. Could diamond's special virtues yield major new opportunities? Its optical properties are exceptional, usually in desirable ways (high refractive indices can create indirect problems). The mechanical properties are truly exceptional, again usually in desirable ways (adhesion can be challenging). The thermal properties are likewise exceptional, with a thermal conductivity that stands comparison with copper. Diamond resists aggressive environments, including extremes of pH. Electron mobility is phenomenal, and electron emission can be excellent. Moreover, diamond can be compatible with silicon electronics, even if the involvement of a second material is inconvenient. But here the problems start. Control of properties is difficult, e.g., it is hard and barely practical to create n-type diamond. Electrical contacts can be tricky. Perception of cost is a further issue: thin film diamond is not expensive, yet the gemstone associations still prove a barrier in major applications.

MATERIALS CONTEXTS: THE KINSHIP OF CARBONS

For almost all performance measures, there is some carbon-based material that performs better than silicon. Yet, as for diamond, it has proved tough to exploit these carbons in electronics, apart from niche applications. Could hybrid carbon-based materials be more successful, that is, should we think less about "diamond" and not more about the *integration* of diamond as one component of carbon electronics [1]? Silicon only became the semiconductor of choice in the 1950s, when the winning feature was an oxide that passivates the surface, acts as an impressive dielectric, and enables high-resolution lithography. But even silicon does not stand alone. Fabrication needs lithography optics and resists, and processing at the anticipated smaller scales may well exploit new electronic excitation methods. Alternative dielectrics and interconnect materials mean new compatibility issues, and there are varied constraints from displays, spintronic components, electron emitters or transparent conductors. Could the varied carbons lead to alternative systems?

The diversity of carbons is striking: diamond, graphites, buckey structures, amorphous carbons, and nanodiamond. Add hydrogen and one has a range of diamond-like carbons and a wealth of organics. These carbon-based materials include small molecules and polymers: impressive insulators, semiconducting and conducting polymers, switchable forms, superconducting and magnetic forms, and intercalates with better conductivity than Cu for a given weight. Such impressive properties may be electronic or photonic, mechanical or thermal. Diamond is superhard, yet diamond-like carbons can have controllable mechanical properties from the viscoelastic to the highly rigid. Photochemistry enables novel processing methods; water-based processing is sometimes possible (alas, not for diamond), and self-organisation of organic molecules on surfaces has been demonstrated.

Current semiconductor technology controls bandgaps and mobilites through alloying and stress. For carbon-based systems, simple band pictures may mislead, though there is scope for control by molecular design and choices of terminations. Blends can create systems that have co-existing n-type (electron transporting) and p-type (hole transporting) behaviour [2]. Texture can be controlled to optimize a mesostructure [3]. The best carbons have impressive, sometimes supreme, performance: the mobility and optical properties of diamond, spin-conserving transport in buckeytubes, and electron emission. Despite these virtues, carbon-based electronics is not in the same league as established silicon technology. But why should carbons compete with silicon in those areas where silicon is supreme? Diamond is not just yet another semiconductor with different standard properties? An alternative view is that carbon electronics should judiciously combine carbons and organics to take the very best properties, avoiding weaker aspects. There is certainly a basis for niche applications, such as combinations of good mechanical and optical behaviour with resistance to corrosion or radiation, or ingenious micromachines.

SOCIAL CONTEXTS: 21st CENTURY NEEDS

Major new applications meet demands from social pressures. There are three clear technology drivers for the 21st century. The first comes from biomedical technologies, where there is wide expectation that novel molecular-scale science will transform the quality of many individual lives. Secondly, there is demand for energy, especially for the developing world, where one must not ignore global constraints or industrial impacts on the biosphere. Thirdly, there are the information technologies, the major enabling technologies, for which new ways to do things will be needed.

THE BIOMEDICAL AND LIFE SCIENCES CONTEXT

Diamond's good *electrochemical* properties give it a niche. Good as they are, diamond's *functional* properties are not unique. Thus, whilst nanodiamond might be used in nanobiomedicine, biomolecules may help diamond more than vice versa. Nature is already good at self-organisation on surfaces, photochemical manipulation and materials modification. Nature is even rather good at managing efficient nanoscale energy transport along protein α-helices. So, despite the niches, it is hard to see a really major opportunity exploiting diamond's functional properties.

What about human-scale biomedical science or technology? Obvious opportunities, like replacing hip joints, seem niche, even though diamond and DLC have excellent tribological properties, and carbon fibre composites can match bone elastic constants and anisotropy to reduce bone wear. Surgeons all have their own favourite choices of implant, and major benefits from materials improvements may need to wait for a new generation of surgeons.

FUSION: OPPORTUNITY AND CHALLENGE

It is an understatement to say that the first wall of a fusion reactor presents materials challenges. Dramatic pictures of plasma disruption events show large local energy releases Could one improve on the graphite that is used in JET, the world's leading fusion experimental facility? Ignoring routine engineering problems,there are four challenges for that critical first inch [4].

First, the wall must *survive,* even under disruptions. This means that a low ablation rate is desirable (the erosion problem); for this, a high atomic binding energy is usually beneficial. There should be a low fragmentation and spalling rate (the dust problem). This requires resistance to thermal shock. Diamond's high thermal conductivity and low thermal expansion are good, but its brittleness is unhelpful. Clearly, diamond has some excellent features, though it is brittle. However, diamond-like carbons can be·viscoelastic, with their degree of viscosity and rigidity controlled partly by their hydrogen concentration and partly by the proportions of sp^2 and sp^3 bonded carbons. Current demands for a conceptual power plant would have a surface energy flux at the divertor of 50 MW/cm^2; that elsewhere at the first wall is less, around10 MW/cm^2. The power density at the first wall is about 55 MW/cm^2.

Secondly, there will be *radiation damage* from 14 MeV neutrons, α and β radiation, photons, and bombardment from hydrogenic species H, D, T in the plasma. The total neutron flux anticipated is 2.10^{11} neutrons per m^2s. Also expected are 2300 atomic ppm H from (n, p) reactions per calendar year and 500 atomic ppm He from (n,α) reactions per calendar year. There will be of order 50 displacements per atom (depending on the material chosen) per full power year. Amazingly, many radiation-related properties are not known. Some of the complexity is discussed in [6], with interesting suggestions that radiation might stabilise diamond [7]. Views of the "informed" field are extraordinarily diverse. One common concern is chemical erosion [8].

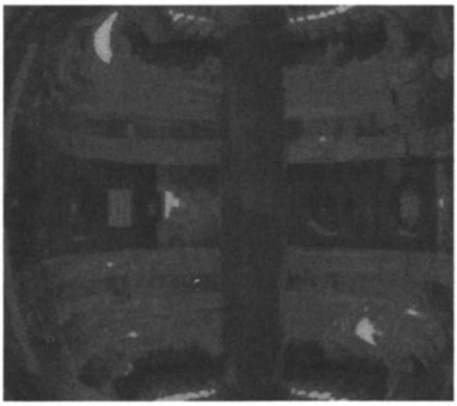

Figure 1. Disruption occurring in the MAST spherical tokomak, showing dramatically the large local energy releases. Figure courtesy Euratom - UKAEA Fusion Association

Thirdly, the strong legal limits relating to the tritium inventory, constrain tritium retention and release. Any tritium should be recoverable, if possible. Fourthly, material from the wall will enter the plasma, but should not harm it. In practice, atoms with high atomic number are bad news, since they can cool (take energy from) the plasma locally. Carbon has Z=6, which is one reason why graphite and carbon composite systems are used today.

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So what might be done? One possibility is to create a "designer carbon," built from various carbon forms, with a chosen micro-structure. Thus the plasma-facing surface might be diamond, to exploit its superb thermal and mechanical properties; there might be a subsurface layer of diamond-like carbon, whose viscoelastic properties might balance the brittleness of diamond and inhibit dust formation and spalling. If tritium is to find its way back into the plasma, one might exploit the hydrogen transport properties of cheap buckeytubes. There have been various suggestions outlined [4]. Diamond's cost in a designer carbon is not prohibitive. Whilst materials for the immediate next generation of fusion devices have been settled [8], many suggestions are close to 1970s-1980s choices. Such choices were very sensible, but do not recognise the alternatives now available. The power plant of 2050 is still at the concept stage. There is time for a serious look at novel options.

EXTENDING THE INFORMATION TECHNOLOGIES

Diamond is unlikely to be an alternative to silicon electronics, even though the diversity of carbons does promise new classes of application. Linking the functionalities of different carbons might be effective, if the best properties of each of the carbon forms were used. Diamond plus compatible organic materials could meet many significant challenges, exploiting the convenience of organics to eliminate diamond's problems. So why are molecules special for electronic applications? Molecules have the right size (1-100nm) to create functional nanostructures; interactions between molecules can enable nanoscale self-assembly (with modest accuracy); molecules can be switched in structure enabling novel functionality (cf., retinal); molecules can be tailored to control electron transport, optical (e.g., colour based on charge transfer) and other properties. However, most molecules cannot stand high temperatures,

Anticipated challenges to silicon stem from needs for greater miniaturization, higher device speed, lower power use, and heat dissipation. Despite porous silicon, silicon-based displays are unlikely to be leaders, nor is silicon the clear material of choice for new opportunities like electronic books. Silicon is challenged in hostile environments, whether high temperatures or electro-chemical conditions. Silicon has a major advantage in know-how: reliable experience at an industrial level and at the state of the art. Present day carbon-based systems often use electrons in mundane ways. Devices based on small organic molecules and on semi-conducting and conducting polymers can perform strongly, and there is a wealth of proposals [9]. Polymeric electrical insulators are standard in everyday life, but with scope for science-based improvements. Designer organics with controlled electronic and ionic processes are the basis of battery and allied systems. But more is needed for carbon-based electronics to go beyond niches.

Do carbon systems offer more sophisticated options? Earlier, [1] I noted five possible ideas. First, interface engineering promises effective control of electron transfer between different (perhaps carbon-based) media. Diamond shows good cold cathode behaviour, and certainly clever things are possible with carbon-based nanotubes, including effective electron emission. A big problem is reproducibility: if you find the ideal buckeytube, it may take a very long time to produce another like it. Secondly, there is plenty of scope to construct mesostructures [3, 10] to form photonic structures, whether by molecular design [11], texturing, blending, self-organisation, or some combination of crosslinking or scission [3]. In such

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mesostructures, many realisations must be examined. It is crucial that features at the atomic, mesoscopic and larger scales are integrated.

1. *Molecular level* e.g., self-consistent → molecular dynamics, tunnelling	2 *Molecular properties* Dependence on length, ↘ charge, curvature;	
3. *Mesoscopic* *structure:* texture, → crosslinks etc	4 *Construct realisations* → Networks with designed statistical properties	6 *Property* *predictions* *for each* *realisation*
5 *Electromagnetic theory* for sub-wavelength films	→	

Figure 2 The linking of energy scales in carbon electronics.

Thirdly, there must be viable ideas for field-effect devices. One carbon might supply the field, and another supply carriers, an especially powerful approach for highly correlated systems [12]. Fourthly, we think of wires to carry power (e.g., interconnects) and optical fibres to carry signals, but we may forget how efficiently the α-helix in protein transfers energy, whether by solitons or otherwise. Mimics of such biological performance might offer value, for life processes are remarkable in the way carbon is exploited. Fifthly, carbons can offer superb optical properties (apart from elusive laser action), not just for conventional devices. Indeed, several proposed quantum computer gates are based on diamond. In all these options, there will be issues at several scale lengths: the atomic and molecular scale; the macroscale associated with optical wavelengths or contacts, and the mesoscale whenever the topology of polymer components or similar are involved. So, as a key question, can carbon-based materials find success in areas that silicon technology cannot address? Here diamond needs simple ways to control dopants: diamond is still far less *convenient* than current semiconductor technology. Whilst diamond needs the advantages of the other carbons, it must be said that carbon electronics may not need diamond.

TAMING THE QUANTUM

There are two implicit questions. First, why seek quantum computing when classical silicon-based computing is so powerful? Secondly, what can diamond do? Quantum information processing [13] encompasses secure communication, database searching, computing, and other information technologies. Quantum information processing has emerged partly from push and partly from pull. The push comes from the success of silicon-based microelectronics and consequent technical demands. The drives to speed, miniaturisation, low energy use and heat dissipation are reaching interesting limits. Semiconductor Industry Roadmap predicts the number of electrons needed to switch a transistor, to fall to only one electron by 2020, making extrapolation tricky.

The pull comes from questions and opportunities raised by quantum physics. How do you describe the state of a physical system? How does the state change if it is not observed? How do you describe observations and their effects? These questions lead to significant reasons for pursuing quantum information processing. How do you describe the state of a physical system?

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Whereas a classical state is often simply state |1> or state |2>, the quantum state is usually given as an amplitude, and can be a superposition of the sort $\alpha|0\rangle+\beta|1\rangle$. The coefficients α, β can embody quantum information. How does the state change if it is not observed? It evolves (deterministically) following the Schrödinger equation, which is a linear wave equation. In essence, we have multiple parallelism because the equation is linear. Quantum parallelism relies on interference to extract a joint property of all solutions of some computational problem. How do you describe observations and their effects? Ignoring the subtleties, the system will collapse with some probability into a single eigenstate; one can know that a measurement has been made. The system "knows" it has been looked at, and this underlies strategies to frustrate eavesdroppers.

The minimum requirements for a quantum computer demand (a) well-defined quantum states as qubits; (b) ability to initialise, i.e., prepare acceptable states within this set; (c) means to carry out a desired quantum evolution (run the device), generally using *universal gates* to manipulate single qubits and to control the entanglements of two or more qubits (control their "quantum dance"); (d) avoidance of decoherence long enough to compute; (e) a means to read out the results (Read process). Implicit are ideas like scalability (the capability to link enough qubits to do useful calculations) and means to avoid or compensate for errors. There are many proposed systems for quantum computing. Yet it is still not certain that a quantum *computer* in the usual sense is possible. Just as friction defeated 19th century mechanical computer makers, so decoherence (loss of quantum entanglement) might defeat large-scale quantum computing, and long decoherence times imply long switching times [14] , though some cases seem achievable [15].

Could diamond offer a practical route to quantum information processing? Many important ingredients have been demonstrated, often using the NV^- nitrogen vacancy centre, sometimes on combination with the substitutional nitrogen centre N_s. The earliest experiments date from the 1980s [16]; subsequent important results [17, 18, 19] include work at room temperature. Some advantages of diamond are clear. Optical transitions in diamond can be very sharp in energy. If electron or nuclear spins are to be used as qubits, then spin-lattice relaxation will lead to decoherence, but is slower when the velocity of sound is high and the spin-orbit coupling small, as in diamond. The spin lattice relaxation time at room temperature of N_s is of the order of a millisecond. One should stress that quantum behaviour is not restricted to low temperatures. Certainly quantum statistics only differ from classical at low temperatures, since the key factor is $\hbar\omega/k_BT$, but quantum statistics relates primarily to systems at or near equilibrium. In quantum information processing, one exploits quantum dynamics, and aims to keep well away from equilibrium. Quantum dynamics involves $\hbar$ in several ways, and quantum phenomena are not directly limited by temperature.

Rather than examine the many approaches, I describe the optically-controlled spintronics ideas of Stoneham, Fisher and Greenland [20] (the SFG approach), who introduced three key concepts. The first was to use spins controlled by laser pulses to give universal gates. Secondly, entanglement achieved through stronger interactions in the electronic excited state of a "control" dopant, with only weak interactions in the ground state. This new concept separates the *storage* of quantum information in qubit spin states from the *control* of quantum interactions. The third new concept was the exploitation of the (usual) disordered distribution of dopant atoms. Dopants do not have to be placed at precise sites: the disorder is needed for *system* reasons. The original proposal suggested devices based on deep donors in silicon. This has advantages because the fabrication and operational steps are almost all ones that have been demonstrated by someone,

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somewhere in the world (this, of course, does not mean creating a working device is trivial). Implementation in silicon seems possible, which could exploit the power of silicon fabrication technology. Diamond could be even better, with N_s as qubits, a system with potential for room-temperature operation that is a acceptably silicon-compatible alternative to those based directly on silicon.

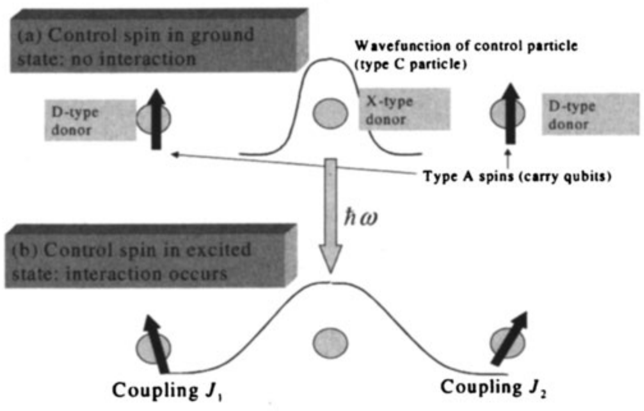

Figure 3. The Stoneham-Fisher-Greenland quantum gate. (a) With the control particle in its ground state, the qubit spins are isolated from one another. (b) Laser excitation creates a delocalised state C, causing indirect interaction between the spins. Classically, the spins precess; quantally, their entanglement is changed, an example of a universal two-qubit gate.

Are there positive answers to the other key questions for diamond-based systems? Are there suitable qubits? The simple N_s donor seems excellent. Are there suitable excited states for control dopants? The simple P donor may prove good. Whilst excited state *energies* of many diamond defects and impurities are known very precisely, there is far less information on wavefunctions. Acceptor effective mass theory works well; donor effective mass theory is largely untested, though there is evidence (albeit indirect) for effective mass states for some deep defects. The GR2-GR8 lines of the neutral vacancy appear to be describably as excitations to effective mass states of an electron bound to the positive vacancy. Can we initialise the qubits? The NV^- centre can be initialised, and quantum information exchanged with N_s even at room temperature

Can a quantum information processor, even a single gate, be run without being overwhelmed by decoherence? We must assess likely decoherence mechanisms. Anything enabling entanglement can cause decoherence (the fluctuation-dissipation theorem implies faster switching means faster decoherence [14]) so *spontaneous emission* can cause loss of entanglement. Spin-lattice relaxation in the ground state would give decoherence (it would affect quantum information storage in the SFG approach) and here, as already observed, diamond is very good, with very long spin-lattice relaxation times for N_s. Excited state processes, like thermal ionisation and two-photon ionisation, could be problems, but probably not for diamond,

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given the energies. Entanglement may also be introduced via the control atoms in the SFG approach, but this can be avoided with the right pulse shapes. Readout can be done in several ways, e.g., that suggested by Stoneham et al [20]; other approaches using NV^- have been demonstrated [17-19]. Thus one possible quantum information processor might be an optically-controlled device with electron spins (say N_s) as qubits, P donors as the control dopants whose optical excitation controls the "quantum dance" (entanglement) of the qubits, and NV^- centres as a means to initialise and perhaps for readout. This approach, one of many solid state proposals, has some special features. Quantum information storage (as N_s spin states) is separated from quantum manipulations (adjustments of entanglement by electronic excitation of controls such as substitutional P). The selection of gates and qubits during processing cannot be done by mere focussing of the light used to excite the controls, which might achieve a resolution of about a micron, whereas the qubits and controls must be separated by about an excited orbital radius, say 10 nm. It is here that the disorder in the system is *desirable.* Excitation energies for each group of control plus qubit groups will vary from one place to another, simply because dopant spacings and relative orientations vary. So individual gates might be operated by a combination of spatial (optical focus) and spectral (choice of wavelength) means. More detailed studies suggest that a likely architecture involves "patches" of perhaps 20 gates near the centre of optically-resolvable regions (perhaps 1-2μm across), linked to other patches by so-called flying qubits. An approach to flying qubits is currently being developed as a patent application, so details are not available for this paper. What is important is that the device could be scalable, i.e., one can recognise ways that quite large numbers of qubits, perhaps several hundreds, might be linked and operated at room temperature.

CONCLUSIONS: BEYOND THE NICHES

Diamond does not lack applications. The new, major, applications are not easily found. One route may be *mix and match* carbon-based electronics. The flexibility, control and cheap processing of organics, whether small molecules or polymers, needs the truly impressive performance parameters of other carbons. So far, efforts to bring these significant advantages together have been limited and short-term, and it is rare to see attempts to draw together the full wealth of carbons in a concerted way. There could be a fusion opportunity. Again, it may be essential to *design* a carbon, taking the best features of different forms in a complementary way to balance resistance to radiation, energy flux, tritium inventory and other factors effectively. Solid state quantum information processing is one area where diamond seems an undeniable leader, possibly good enough to win though.

ACKNOWLEDGMENTS

This work was supported by EPSRC through its Basic Technologies and Carbon-Based Electronics programmes, and also by Culham Laboratory. I am indebted to many of my colleagues for their input.

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