Crystalline Carbon and Silicon: Covalent or Ionic?

the general science journal

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Abstract

Diamonds and silicon wafers are prized materials that share a common crystal structure. Tetrahedral atom interactions are the basis for their properties: hardness, thermal conductivity, electrical non-conductivity, etc. sp^3-Hybrid orbitals provide the current explanation for the interatomic "bond" connections. These covalent bonds, however, do not provide an adequate mechanism for these materials acting as semiconductors. Ionic bonding between atoms with the crystal lattice fully connected via overlapped, but "unoccupied", orbitals does provide a logical structure to explain how semiconductor doping works, however.

Introduction

A crystal or crystalline solid is a solid material whose constituent atoms, molecules, or ions are arranged in an ordered pattern extending in all three spatial dimensions. Ionic crystals can form upon solidification of salts, either from a molten fluid or upon crystallization from a solution. Ionic crystals with electrostatic attractions are noted for having high melting points and being hard, brittle and good electrical conductors 'in the molten state'. A diamond is a crystal of tetrahedrally aligned carbon atoms in a variation of the face centered cubic structure called 'the diamond cubic crystal structure'. The network lattice is described as covalently bonded, sp^3, atoms that give diamonds the highest hardness of any bulk material.[1] Silicon, as would be expected from its position in the periodic table, also crystallizes in a diamond cubic crystal structure[2], and, unlike diamond, can be fabricated into large spheres.[3]

This brief paper questions the logic of the physical properties for these materials being the result of covalently bonded atoms in the crystals. A few physical facts about diamond carbon and silicon will help set the stage.

Diamond Carbon

Diamond carbon melts at 4440°C. The interatomic distance[4] is 1.54Å with a cubic cell unit[5] of 3.56683Å containing 8 atoms (8 corners*1/8, 6 faces*1/2 and 4 inside*1). It has very high thermal conductivity (2000+ $W \cdot m^{-1} \cdot K^{-1}$; compare to gold at 318).[6] Most materials that conduct heat well have a valence band of free electrons which serve to transfer the heat.[7] On the other hand, diamond carbon is an electrical insulator with a very low electrical conductivity[6] (10^{-13} $\Omega^{-1}m^{-1}$; compare to gold at 4.5×10^7). The first ionization of an electron from carbon[8] is 1087 $kJ \cdot mol^{-1}$ and internal electric charges do not flow freely under the influence of an electric field. However, synthetic diamonds doped with boron are p-type semiconductors, while those doped with phosphorous are n-type. Thin-film diamond n-type semiconductor wafers are now being generated.[9] Silicon wafers are the state-of-the-art in the semiconductor business. However, the much higher melting point of diamond carbon versus that of silicon[2] (1414°C) provides an impetus for replacing silicon.

Silicon Crystal/Wafers

Silicon crystals are strong, but very brittle and prone to chipping. The interatomic distance[10] is 2.22Å with a cubic cell unit[2] of 5.430710Å containing 8 atoms. The thermal conductivity[2] is much lower at 149 $W \cdot m^{-1} \cdot K^{-1}$than that of diamond carbon. While the electrical conductivity[11] at 1.56×10^{-3} $\Omega^{-1}m^{-1}$ is much higher than that of diamond, but silicon is hardly a conductor. The first ionization of an electron from silicon[8] at 787 $kJ \cdot mol^{-1}$ is 72% that of carbon, but a mere 7% greater than that of magnesium[8] (738 $kJ \cdot mol^{-1}$). Unlike the difficulty of forming diamond carbon in large sizes, large cylindrical ingots of the high purity (99.9999999%), crystalline silicon, needed for integrated circuit making[2], can be produced by pulling a seed crystal from a 'melt' in the Czochralski process.[12] Silicon wafers are generally not 100% pure silicon, but are doped with tiny amounts of a particular element (<1 atom of additive for >10,000 crystal cell units of silicon!)[13] to make a wafer of the desired semiconductor type and responsiveness. These added atoms greatly increase conductivity and allow the electrical behavior to be set. Like the time-honored cleavage of diamonds along lattice planes to produce brilliant gems, the crystalline silicon ingot is cut into wafers. Scoring the wafer along cleavage planes allows billions of individual circuits to be placed on an average wafer.

Factors to be explained by the Atomic Orbital Structure

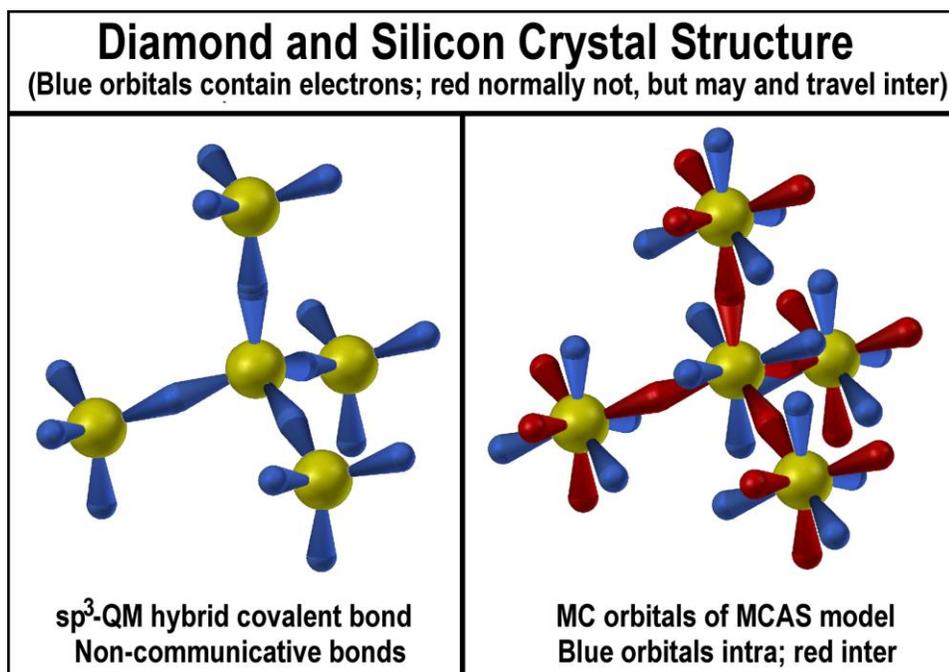| Dependency	Factor	Carbon	Silicon
Atom Locations	Unit cell structure	Every atom tetrahedrally is surrounded by a nearest neighbor	
	Mechanically strong	Strong, symmetrical, atom interactions are all working together	
	High melting		
	High thermal conductivity	Very rigid crystal matrix gives strong transfer of energy from atom to atom and thus across the crystal; there is no electron flow	3.5x the cell volume of diamond; more room for flexing means less direct energy transfer to adjacent atoms and thus less across the crystal
	Sharp Cleavages	Perfect 111 crystal planes slide easily with a sharp blow	
	Brittle	Diamond hard; tight atomic network	1.44x diamond inter nuclear distance – much weaker crystal planes
Electron Placement And Flows	Unit cell structure	Every atom is tetrahedrally surrounded by a nearest neighbor	
	Electrical insulator	No electron flow from atom to atom; electrons are tightly bound	Silicon is a very weak natural semiconductor; electrons are less tightly bond than in diamond
	Semiconductor behavior	Electron flow through atomic matrix when elements that provide "holes" or "electrons" are present in minuscule amounts; how?	

Electron Orbital Models

The currently accepted electron orbital model of atoms is the spdf-QM model. The figure at the right indicates the sp^3-QM hybrid that is used to address the atomic interactions of diamond carbon and silicon. Included in the figure are the corresponding MC orbitals of the MCAS model. A description of the two is provided elsewhere.[14] Both provide tetrahedral orientation of orbitals with the spdf bonding orbitals having been formed by "hybridizing" the spherical s and hour-glass p atomic orbitals. The MC orbitals are not hybrids as they are those of the free atomic element. The primary distinction between the sp^3-QM hybrid and the MC orbitals is what will house the 4 outer ("valence") electrons and what will form bonds. The sp^3-QM hybrid has a singular way to house electrons and form bonds with electron spin-pairing. The mirrored MC orbital pairs allow electrons and bonds to be handled jointly or independently.

spdf-QM vs MCAS

sp³ Hybrid   MC Orbital Pair
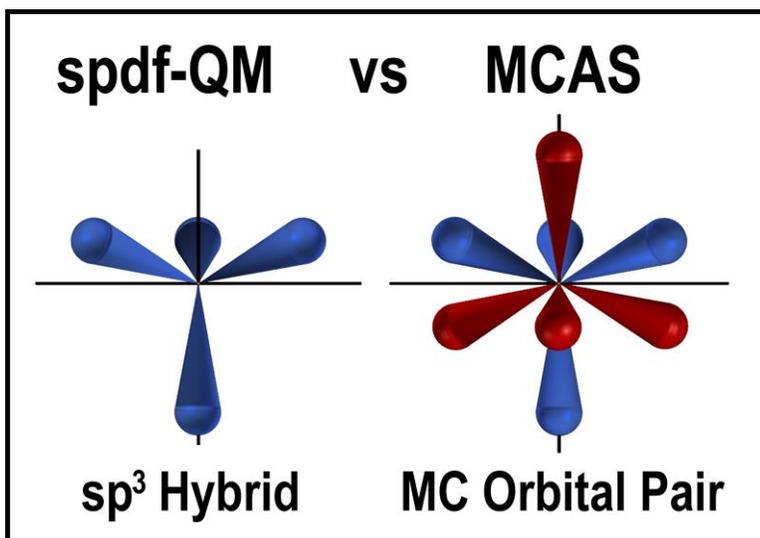
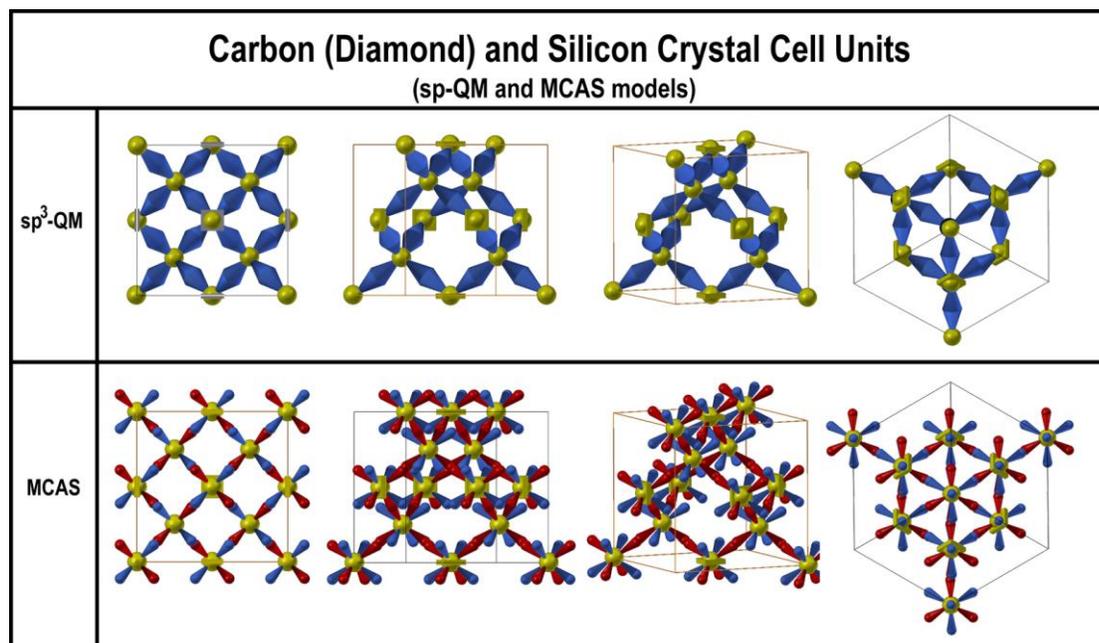# Addressing the Tetrahedral Arrangement of Diamond and Silicon Atoms

The figure at the right illustrates how the two models address the tetrahedral interaction of a diamond carbon or silicon atom with its four nearest crystal neighbors. Both show staggered (minimal electrostatic repulsions) configurations for the electron containing orbitals. The sp^3-QM model has the electrons shared as spin-reversed pairs on the axis between two atoms in what is called a "covalent bond". The MCAS model has no electrons shared by atoms as the atoms protect themselves first; thus, there are no electrons on the axis between any two atoms in the perfect crystal. The "bonding" in the MCAS model would be described as "ionic". Electrostatics of such bonds have been present elsewhere.[15]

Diamond and Silicon Crystal Structure
(Blue orbitals contain electrons; red normally not, but may and travel inter)

sp³-QM hybrid covalent bond
Non-communicative bonds

MC orbitals of MCAS model
Blue orbitals intra; red inter

In the sp^3-QM model, each sp^3 orbital is independent of the others; thus, electrons do not flow from one orbital to another. This is used to describe why diamond carbon is such an excellent electrical insulator. The same can not be said about its explanation of the semiconductor behavior produced by <80 "hole" or "electron" atoms for every million unit cells! It also does not explain why silicon is a natural, but weak, semiconductor.

In the MCAS model, the red, unfilled, but overlapped orbitals provide a continuous "tunnel" network throughout the crystal. With a high, 1st ionization energy, carbon atoms hold their own electrons very tightly. With no readily available electrons, diamond carbon is not a natural semiconductor. With doping, the "tunnel" network allows diamond carbon crystals to become semiconductors. Silicon, on the other hand, has a lower, 1st ionization energy. With the release of just a few electrons into the "tunnel" network, silicon becomes a natural semiconductor. Doping that places "holes" and "electrons" in the "tunnel" network allows silicon to become the state-of-the-art semiconductor used in integrated circuits.

The figure on the right shows the crystal cell unit according to the two orbital models. Four of the corner atoms are omitted so that the remainder is easier to view.

Carbon (Diamond) and Silicon Crystal Cell Units
(sp-QM and MCAS models)

3

REFERENCES

[1] http://en.wikipedia.org/wiki/Crystal

[2] http://en.wikipedia.org/wiki/Silicon

[3] Large silicon spheres are being produced in an effort to define the

kilogram (*Scientists look to define kilogram with a super-round silicon sphere*, http://ceramics.org/ceramic-tech-today/scientists-look-to-define-kilogram-with-a-super-round-silicon-sphere)
  and
Avogadro's Number (*Avogadro's Number Needs A Simple Expression*, http://pages.swcp.com/~jmw-mcw/binary_mole.htm)

[4] http://en.wikipedia.org/wiki/Bond_length

[5] http://en.wikipedia.org/wiki/Material_properties_of_diamond

[6] http://en.wikipedia.org/wiki/List_of_thermal_conductivities#cite_note-EngineeringToolbox-858-11

[7] http://en.wikipedia.org/wiki/Helium

The thermal conductivity of helium II (a liquid) is greater than that of any other known substance several hundred times that of gold. The flow of heat is said to be governed by equations that are similar to the wave equation used to characterize sound propagation in air. (Presumably a shock wave through very closely "connected" atoms; helium atoms would have multiple 'bonding'; how? – jmw)

For orbitals that permit multiple bonding interaction of first period elements, see the references below:

a: *Electron Orbitals for Ortho and Para Helium*,
http://pages.swcp.com/~jmw-mcw/electron orbitals for ortho and para helium.htm

b: *Hydrogen Bonding and Orbital Models*,
http://pages.swcp.com/~jmw-mcw/Hydrogen Bonding and Orbital Models.htm

[8] http://en.wikipedia.org/wiki/Molar_ionization_energies_of_the_elements

[9] *Argonne licenses diamond semiconductor discoveries to AKHAN Technologies*,
http://www.anl.gov/articles/argonne-licenses-diamond-semiconductor-discoveries-akhan-technologies

[10] http://www.webelements.com/periodicity/

[11] http://en.wikipedia.org/wiki/Electrical_resistivity_and_conductivity

[12] http://en.wikipedia.org/wiki/Wafer_(electronics)

[13] http://en.wikipedia.org/wiki/Doping_(semiconductor)

[14] *PARSING THE spdf ELECTRON ORBITAL MODEL*,
http://pages.swcp.com/~jmw-mcw/Parsing the spdf electron orbital model.htm

[15] a) Joel M Williams, *Understanding the Bonding of Second Period Diatomic Molecules*, click image for url
(Ever wondered how positive charge-forces are transmitted throught the electron orbitals of the cations of crystals, like NaCl, to give them their positiveness? The cations are not likely to be solid spheres of simple net positive charge on the exterior, even if it is easier to think of ions as positive and negative balls.)
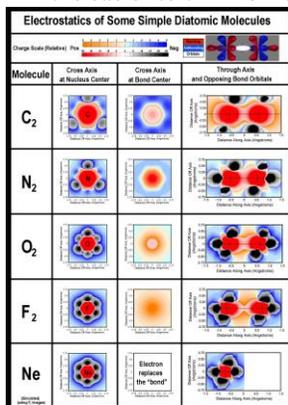
b) Joel M Williams, *Modeling the MCAS Way*,
http://pages.swcp.com/~jmw-mcw/science; http://arxiv.org/html/physics/9902046v2

c) Joel M Williams, *Challenging Science*, AuthorHouse, July 25, 2005,
http://www.amazon.com/Challenging-Science-Joel-M-Williams/dp/1420842382