Electron Emission from Diamondoids: a DMC Study

Neil D. Drummond
Andrew J. Williamson
Richard J. Needs
and Giulia Galli

August 23, 2005

Semiconductor Nanoparticles for Optoelectronic Devices (I)

- The *optical gap* (OG) is the difference between the ground-state and first-excited-state energies of a molecule.

- *Quantum-confinement* (QC) effects should elevate the OGs of nanoparticles of group-IV elements above the corresponding bulk band gaps.

- The effect is caused by the increase in the KE of a state when it is spatially confined.

Semiconductor Nanoparticles for Optoelectronic Devices (II)

- Films of nanoparticles can be placed on the surfaces of photodiodes and LEDs.

- Si and Ge nanoparticles have been studied extensively, as they can be integrated with existing device fabrication techniques.

- Until recently, carbon nanoparticles have been more difficult to synthesise and study.

- The diamond band gap (5.47 eV) is in the UV range.

- QC might push the OGs of carbon nanoparticles even further into the UV range, allowing UV sensors to respond to higher frequencies than ever before.

Semiconductor Nanoparticles for Electron-Emission Devices (I)

- The electron affinity (EA) of a molecule is the energy released when the molecule and a free electron form an ion.

- The EA of a semiconductor or insulator is the difference between the conduction-band minimum and the vacuum level.

- Some hydrogen-terminated diamond surfaces have negative EAs.

- So hydrogen-terminated carbon nanoparticles should have low or negative EAs.

Semiconductor Nanoparticles for Electron-Emission Devices (II)

- Conventional TV tubes involve heating a metal element to produce electrons, accelerating them down a vacuum tube using an electric field, and moving the resulting beam across a phosphor screen using magnetic fields.

- Would like to have a large, light, flat, power-efficient display device that doesn't have the limitations of LCD screens (e.g., slow response time, limited viewing angle).

- Idea: develop *field emission devices*, in which each pixel has its own cold electron-emitter, with the electrons being pulled off the emitter by an electric field.

Semiconductor Nanoparticles for Electron-Emission Devices (III)

- The strength of electric field required is most serious problem with this technology.

- Materials with negative electron affinities will readily emit conduction electrons.

- Hence the electric field required to pull the electrons off such materials would not need to be especially strong.

Diamondoids

- Hydrogen-terminated carbon nanoparticles are called *diamondoids*.

- Chemists from ChevronTexaco have isolated diamondoids from petroleum.

- Crystals of diamondoids have been grown.

- Functional groups have been added to diamondoids.

- Polymers of diamondoids with up to 10^6 repeat units have been produced.

Experimental Results

- An XANES study found substantial QC in diamondoids of up to several nanometres in diameter.

- A NEXAFS study found no evidence of QC in such nanoparticles.

- No experimental studies of electron affinities of carbon nanoparticles?

- Several technologically important questions, but the experimental results are contradictory or nonexistent.

- Accurate first-principles simulations are clearly required!

Previous DFT Simulations

- DFT OGs are always underestimated: this is the well-known "band-gap" problem.

- One DFT study predicted that the OGs of diamondoids fall off rapidly as their diameter increases.

- At 1 nm, the OGs were predicted to lie below the band gap of diamond.

- Another DFT study found that the OGs of the same molecules are substantially higher than the diamond gap.

- No DFT results for electron affinity?

- More accuracy required? Use QMC!

The QMC Calculations (I)

- C and H pseudopotentials were used.

- The Troullier-Martins C psps from the ABINIT web site give smaller variances and more stable DMC than the Hamann ones.

- Very large boxes (side-length 35–50 a.u.) and plane-wave cutoff energies (35–50 Ry) were used for the DFT calculations.

- Orbitals were represented by splines on a grid in real space.

- The time step was 0.02 a.u.; the resulting errors are negligible.

The QMC Calculations (II)

- Changing the XC functional used to generate nanoparticle geometry and trial wave function altered the DMC OG by 0.3 eV.

- The HOMO was replaced by the LUMO in the spin-down Slater determinant to give the excited-state wave function.

- Typically, this introduces an error of 0.1–0.2 eV into the excited-state DMC energy.

- Overall, the error in the DMC OG is expected to be about 0.5 eV.

Optical-Gap Results

- The DFT OGs are lower than the DMC gaps by about 2 eV.

- The DMC OG decreases rapidly with cluster size, falling below the bulk gap at a size of about 1 nm in diameter.

- Not quite what was hoped for!

- Differs from the behaviour of the OG in Si and Ge nanoparticles.

- DFT is qualitatively (not quantitatively) correct in all cases.

- Why does the QC model apply to Si and Ge nanoparticles, but not carbon ones?

Nature of the HOMO and LUMO for Diamondoids (I)

- The HOMO is located on the atoms and bonds within the nanoparticle.

- LUMO is a diffuse surface state for diamondoids; this not the case for Si or Ge.

- The HOMO evolves into the valence-band maximum as the cluster size increases.

- The LUMO does **not** evolve into the conduction-band minimum. It is like a surface or impurity state within the band gap.

- The LUMO is clearly not confined.

Nature of the HOMO and LUMO for Diamondoids (II)

- The LUMO is essentially unbound; this suggests EA will be small or negative.

- The disagreement between previous DFT results arose because one group used an inadequate Gaussian basis set to describe the diffuse LUMO. The LUMO was therefore artificially localised, producing a spurious QC effect.

Electron Affinities of Diamondoids

- DFT and DMC electron affinities and ionisation potentials are in close agreement.

- The electron affinities are negative, as was hoped.

- Diamondoids are therefore candidates for use as low-voltage electron emitters.

- Other candidates exist. Whether diamondoids turn out to be the best option depends on how cheaply and easily they can be produced.

Future Work

- I'd like to study the effect of adding hydroxyl and carboxyl groups to diamondoids.

- I'd like to study polymers of functionalised diamondoids.

- Is the LUMO still delocalised? What happens to the OGs and electron affinities? What are the elastic properties of diamondoid polymers?

- *Buckydiamonds* are recently discovered carbon molecules with diamond-like interiors and fullerene-like exteriors.

- I hope to explore the optical and chemical properties of these new materials.