Nanocarbons as Potential Thermoelectric Materials

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The dawn of the age of solar power brings with it the realization that the building of multimegawatt central station power plants to sustain a global industrial civilization will require enormous capital investments. For this reason, economic considerations will dominate to an extraordinary degree the choices made in the production of electricity from such plants. Among the important factors that bear on economics are site location, maintenance costs, and energy conversion efficiency. Remote sites will require reliable operation at high energy conversion efficiencies for extended periods of time with minimal maintenance.

Thermoelectric materials have functioned superbly in unattended, maintenance free stressful environments to generate electrical power for spacecraft such as Cassini,Galileo and Voyager, in the latter case for a period exceeding twenty years. Despite decades of intense development efforts, current state of the art materials are constrained to conversion efficiencies of 8-12% . Formidable, well-recognized challenges appear to forbid the scaling of this barrier using bulk materials.

A new approach using nanomaterials has been proposed which promises to overcome the hitherto intractable problems preventing the efficient direct conversion of heat to electricity. Because of their low dimensionality, nanomaterials can achieve high thermopower due to high densities of states at the Fermi level while thermal conductivity can be held to low values due to grain boundary phonon scattering. In addition, recent theoretical work has shown that inhomogeneous doping of superlattice nanowires could result in “reversible” electron transport leading to figures of merit, ZT, between 5-10. Such materials could in principle convert heat to electricity directly with at least 40% efficiency thus becomimg competitive with rotating machinery.

The premium set on high conversion efficiency means that the highest achievable ZT values must be coupled with Carnot efficiencies of 70-80% achievable at operating temperatures of 800-1000°C. Most nanomaterials tend to lose their nanocrystallinity at high temperatures because diffusional processes are strongly enhanced by the large surface to volume ratios. Therefore one must chose candidate nanomaterials for high temperature thermoelectric applications that maintain their favorable “quantum” properties at the operating conditions specified above. Diamond and graphite, because of their strong covalent bonding, have very high activation energies for diffusion. For this reason, nanocarbons such as ultrananocrystaline diamond (UNCD) and carbon nanotubes (CNT’s) preserve their nanostructural properties and maintain stable interfaces even at temperatures exceeding 1000°C.

In this talk, I will discuss some properties of self-assembled self-aligned UNCD/CNT self composites that would make them potentially suitable as a new class of high ZT, high temperature thermoelectric materials for the efficient conversion of solar heat to electricity.

Spin resonance as well as magnetoresistance data suggest that electron delocalization is induced by the interaction of nitrogen sigma orbitals with pi-orbitals on grain boundary carbon atoms when UNCD is grown with the addition of nitrogen to the synthesis gas. Tight binding density functional calculations on such materials show that a high density of states is found in the band gap of UNCD near the Fermi energy. The extraordinary n-type electrical conductivity of UNCD can therefore be rationalized on the basis of a variable range hopping mechanism which is also supported by detailed electrical conductivity and Hall effect measurements.

Covalently bonded composites of UNCD with CNT’s can be expected to display further increases both in the electrical conductivity and in the density of states compared to UNCD alone. Such a conclusion is based on the fact that electron transport in CNT’s can be ballistic and on the recent surprising finding that pentagon, heptagon and octagon defects created by the reaction of carbon dimer molecules with CNT’s introduce sharply peaked electronic states near the nanotube Fermi energies. Low measured thermal conductivities combined with the favorable electrical conductivities and densities of electronic states likely to be exhibited by UNCD/CNT composites can hopefully lead to favorable thermoelectric properties that can be maintained even at high temperatures.

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