

Configurational, electronic entropies and the thermoelectric properties of nanocarbon ensembles

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Reaction of disperse ultrananocrystalline diamond (UNCD) and mixtures of UNCD containing 10%–20% nanoboron carbide (B_4C) with methane gas at temperatures near 1200 K results in mechanically rigid compacts called nanocarbon ensembles (NCE) and boron-doped NCE, respectively. Seebeck coefficient and electrical conductivity results lead to strongly temperature dependent power factors that increase 30–40 fold for boron containing ensembles compared to undoped material. It is likely that boron substitutional doping of nanographite crystallites results in a multiplicity of electronic states within a narrow energy band around the Fermi level leading to an increase in configurational electronic entropy. © 2008 American Institute of Physics.

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The ongoing quest for highly efficient thermoelectric materials has centered in recent years on nanomaterials. In part, this is due to at least two circumstances. First, phonon scattering at grain boundaries tends to decrease thermal conductivity and second, low-dimensional materials can in principle lead to an enhanced density of states at the Fermi level. Employing these concepts, impressive values as large as 2.5 for the figure of merit (ZT) indeed have been achieved with superlattice structures, for example.¹ In order to have a meaningful impact on global electricity generation, however, one will have to be able to reach at least $ZT=5$ so as to be competitive with state-of-the-art power conversion efficiencies of 30%–40%. Limits imposed by various inefficiencies, including the Carnot efficiency which limits the performance of all heat engines, lead to an important often overlooked criterion in selecting a thermoelectric material capable of attaining maximum conversion efficiencies near 40%. Even with a $ZT=5$ material, a temperature differential of 1000 K between the cold and hot ends of a thermopile is required. Therefore, with the cold end maintained at the reasonable value of 400 K, the hot end must be heated to and continuously operate at 1400 K. If the thermoelectric elements are to be constituted of nanomaterials, it is imperative that their nanocrystallinity be maintained at high temperatures so as to preserve their desirable “quantum” properties. In the event, suitable thermoelements must be chosen from the list of nanocrystalline refractory materials that can be shown to not recrystallize at the high operating temperatures. Such a list appears to be severely limited in the number of candidates that can meet this requirement particularly since the high surface to volume ratio of nanomaterials in fact tends to lower the recrystallization temperatures characteristic of bulk materials.

Carbon is one of those candidate materials because its high Debye temperature confers on it a very high recrystallization temperature. This desirable property also extends to the family of nanocarbons including ultrananocrystalline diamond (UNCD) which occurs in both thin film² and dispersed

powder forms.³ Thin films of UNCD become highly n -type electrically conducting when nitrogen is incorporated into their ubiquitous grain boundaries which are largely constituted of sp^2 bonded carbon.⁴ In turn, the grain boundaries have been shown to partake of some of the characteristics of transacetylene.⁵ The electrical properties of the films remain unchanged even when cycled between ambient temperatures and at least 1200 K,⁶ and their thermal conductivities are low [0.06 W/cm K (Ref. 7)], thus making them of interest as thermoelectrics. However, the concern of the present paper is nanocarbons based on the relatively much more abundant disperse form of UNCD. The starting materials are UNCD powders composed of 3–5 nm crystallites that can readily be formed into compacts by reaction with methane gas at elevated temperatures.⁸ The microstructure of the compacts is currently not well understood. Our working hypothesis, partially confirmed by preliminary high resolution transmission electron microscopy results,⁹ suggests that covalent bonding between several nanocarbons including UNCD, carbon onions, carbon nanotubes, and nanographite resulting in mechanically stable and electrically conducting self-composites is brought about when methane reacts with the disperse diamond crystallites. This aspect of the work involving the synthesis of materials which we term “nanocarbon ensembles” (NCE) will be described below in more detail. Importantly, low-level substitutional doping with boron (boron-doped NCE) enhances the thermopower of the ensembles very sub-

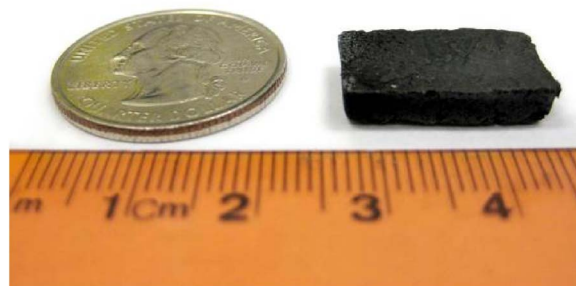


FIG. 1. (Color online) Photograph of the nanocarbon ensemble (NCE) as synthesized.

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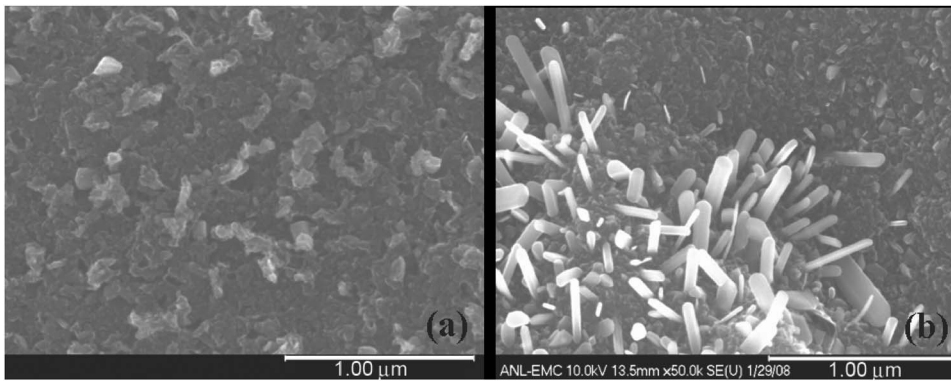


FIG. 2. Scanning electron microscope (SEM) micrographs for (a) NCE and (b) boron-doped NCE prepared with 20% B_4C .

stantially compared to the low thermopower measured by us and others⁸ on the undoped material (NCE). Much higher thermopowers are likely to be observed as higher doping levels are reached on going to temperatures where diffusional processes become kinetically favorable.

Here, we present initial results obtained by going to processing temperatures of 1200 K. Disperse nanodiamond powders¹⁰ either pure UNCD or mechanically mixed with 10 wt % of nano B_4C (Ref. 11) were placed in $20 \times 10 \times 5$ mm highly oriented pyrolytic graphite crucibles and after an initial compaction step treated with methane gas in a quartz vessel heated in several intervals from ambient temperatures to 1200 K in a tube furnace. The contents of the crucibles gained between 70% and 100% in weight with the greatest change occurring between 950 and 1050 K. For both UNCD and UNCD+ B_4C this procedure resulted in the formation of mechanically rigid compacts with densities of 1.5–1.7 g/cm³ (Fig. 1). Their scanning electron microscope (SEM) micrographs are shown in Figs. 2(a) and 2(b), respectively. Note the formation of nanorods in Fig. 2(b) which only occurs in B_4C containing ensembles after reaction with methane in the temperature range of 1000–1400 K. The presence of the nanorods does not alter either the Raman or the x-ray diffraction (XRD) scattering results. On the basis of weight gain data, we conclude that a heterogeneous reaction involving methane, UNCD and B_4C converts the latter to BC_3 . The rods disappear beginning at temperatures of 1500 K presumably because BC_3 decomposes to B_4C and C. Kouketakis *et al.* proposed a graphite structure for the material but there are no structural data¹² possibly because the crystallite size is only a few nanometers. The Raman spectra of ensembles with and without boron are dominated by the so called “G” and “D” bands of graphitic carbon. Although the ensembles roughly contain equal amounts of sp^2 and sp^3 bonded carbon, the very large scattering cross section of the former overwhelms the much less intense scattering due to the latter. XRD measurements of a NCE sample are presented in Fig. 3(b) together with the original diamond nanopowder in the dispersed form [Fig. 3(a)]. The XRD spectra show that nanodiamond is the majority constituent even after reaction with methane, as revealed by the intensity of the $\langle 111 \rangle$ reflection located between 42° and 44° . The increase in weight can now clearly be seen as due to the formation of sp^2 bonded nanocarbon evidenced by the feature between 23° and 26° . The location and width of this band is virtually identical with that due to the formation of polyhedral nanographite crystallites, as observed when UNCD powder is graphitized at temperatures higher than 1200 K.¹³ We suggest that highly reactive UNCD surfaces enable a heteroge-

neous reaction of methane to occur resulting in the formation of largely sp^2 bonded grain boundaries surrounding the UNCD crystallites thus binding them together into a rigid network.¹⁴

The Seebeck coefficients (S), electrical conductivities (σ), and thermal conductivities (κ) of the compacts were measured using an apparatus designed and built in our laboratory employing Keithley voltage and source meters. Ohmic contact of the compacts with metal electrodes was easily established by mild pressurization of the latter. The thermal conductivity of the compacts between 300–600 K was estimated to be in the range of 0.02–0.05 W/cm K using a comparative measuring technique. The salient result of our measurements is graphically displayed in Fig. 4. The power factor is seen to be strongly temperature dependent and increases by more than a factor of 30 at 1000 K for compacts synthesized by addition of 10% B_4C compared to nonboron containing compacts.

Boron doping of diamond¹⁵ as well as of carbon nanotubes¹⁶ is known to result in an increase in the Seebeck coefficient. Presumably boron π states induce an acceptor-like feature near the top of the valence band.¹⁷ We believe that the increase in thermopower observed in the NCE studied here is due to boron atoms substituting for carbon in UNCD as well as in nanographite crystallites. Density functional calculations are in progress to elucidate increases in the density of states near the Fermi level due to changes particularly in the nanographite electronic structure resulting from boron substitution.¹⁸ Our method of synthesis in all likelihood gives rise to a statistical distribution of boron at-

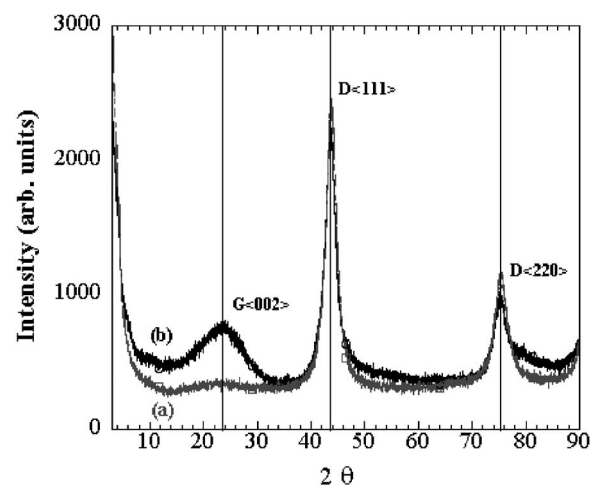


FIG. 3. XRD spectra for (a) the original powder and (b) NCE.

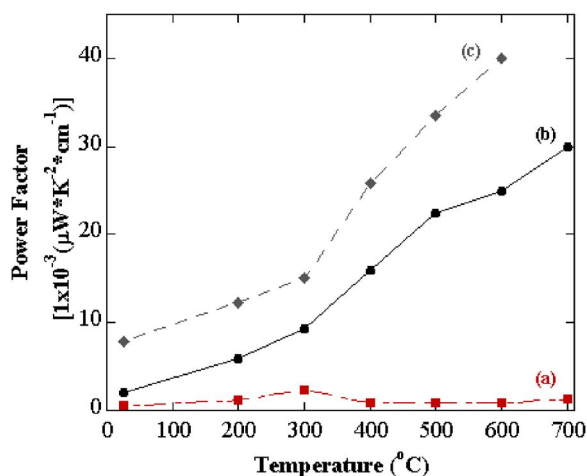


FIG. 4. (Color online) Power factor for (a) NCE, (b) boron-doped NCE prepared with 10% B₄C, (c) boron-doped NCE prepared with 20% B₄C.

oms in both lattice and edge sites of nanographite with the establishment of a multitude of geometric configuration. A multiplicity of electronic states within a narrow energy band near the Fermi level is a likely concomitant of this situation. The ensuing enhancement of configurational electronic entropies is a prerequisite for the observation of large Seebeck coefficients. An understanding of the factors controlling the magnitude of the Seebeck coefficient is particularly important because it enters the expression for the ZT as the square of the quantity. The approach taken here is unique in the fact that it explicitly recognizes the dramatic effect of boron atoms (as well as those of certain other elements) as substituents for carbon on what may be called the “resonance” structure of a graphitic lattice. Such substituents cause changes of several electron volts in the resonance energy of graphene sheets, for example. The substantial effect on the energetics of the molecular orbitals can be calculated by quantum mechanical computer modeling. One can therefore elucidate the effect, for example, of changes in molecular orbital ordering due to the placement of two boron atoms relative to each other on various lattice points in exquisite detail.¹⁸ In this way, a set of density of states near the Fermi level can be separately obtained for each boron configuration with each individual configuration being responsible for a discrete set of electronic states, each with its characteristic multiplicity.

As already stated, the boron doping levels in our samples are very low, of the order of 0.01% based on extrapolation of Lowell’s solubility data to 1200 K.¹⁹ By heat treatment of the NCEs above 2300 K, boron doping levels of 1%–3% will be reached.¹⁹ At the same time, UNCD converts to nanographite³ under these temperature conditions thus crucially increasing the sp^2/sp^3 ratio in the ensembles. The increase in boron doping level is expected to lead to an order of magnitude increase in the Seebeck coefficient. Such a re-

sult would be consistent with large increases in Seebeck coefficient as a function of boron doping observed in polycrystalline diamond.¹⁵ On the other hand, a large increase in the fraction of sp^2 bonded carbon due to conversion of UNCD to nanographite is expected to lead to an order of magnitude increase in electrical conductivity. The two combined effects, if realized, would yield ZT values in the range of 1–5.

Inhomogeneous doping has been proposed in order to achieve “reversible” performance.²⁰ This means that by isentropically operating a thermoelectric heat engine one should be able to more closely approach the Carnot efficiency. Isentropic operation requires one to be able to dope the thermoelectric material in an inhomogeneous fashion. Interestingly, the NCE in a straightforward way lend themselves to achieving optimal inhomogeneous n - or p -type doping concentration gradients by simply carrying out the procedure along a predetermined temperature gradient. In the event, the ZTs of the NCE could still be further improved.

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