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Synthesis and Characterization of Semiconducting Boron-doped Amorphous Carbon Materials Using an Organic Boron Compound as a Precursor

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Boron-doped amorphous carbon was synthesized by polymerizing naphthalene and triphenylborane with subsequent heat treatment by spark plasma sintering. The boron-doped carbon material has negative Seebeck coefficient ($-0.22\,\mathrm{mV\,K^{-1}}$), which indicates the carbon material functions as an n-type semiconductor.

The allotropes of carbon materials such as graphene, fullerenes, and carbon nanotubes have attracted increasing attention due to their novel physical and unusual electronic properties. These graphitic materials, which consist of sp^2 hybridized carbons, have been employed as field effect transistors, field emission electrodes, and solar cells.[1] On the other hand, thin films of amorphous carbon (*a*-C) that contain mixed configurations of threefold (sp^2) and fourfold (sp^3) coordinate sites have a number of useful properties, such as high dielectric strength, chemical stability,[2,3] and a tunable band gap by adjusting the sp^2 and sp^3 bond ratios. Applications of *a*-C in the field of semiconductors are wide.[4] In order to modify the electronic properties of *a*-C, heteroatoms such as N and B are often used as dopants, producing n-type and p-type semiconductor behavior, respectively.[5,6]

Organic boron compounds are more stable and less toxic than B-source materials such as diborane or boron chloride and are expected to be efficiently incorporated into carbon frameworks. In this study, B-doped *a*-C semiconducting materials that exhibit an n-type semiconducting behavior were prepared using an organic boron compound.

B-doped *a*-C materials were synthesized by polymerizing naphthalene and triphenylborane in the presence of $AlCl_3$, followed by heating the resulting carbon precursor by spark plasma sintering (SPS). Synthesis involved the following two-step procedure: 7.5 g of naphthalene, 0.78 (0.5 atom % B-doped sample) or 1.96 g (1.0 atom % B-doped sample) of triphenylborane, and 4.0 g of $AlCl_3$ were mixed and heated at 673 K for 50 h under nitrogen gas flow. The obtained carbon precursor (powder) was washed repeatedly with ethanol and tetrahydrofuran to remove residual $AlCl_3$. The resulting carbon precursors were pressed under 50 MPa in a spark plasma sintering apparatus (SPS515S, SPS Syntex Inc.). The samples were heated to 873 K at 100 K min^{-1} and held for 10 min to produce sample pellets (diameter: 15 mm, thickness: 2 mm).

Figure 1A shows Raman spectra of the nondoped and B-doped *a*-C materials. The peaks observed at 1580 and 1350 cm^{-1} are attributed to the *G* (stretching mode of graphite) and *D* (breathing mode) bands, respectively. There is no difference in the ratio of the *G* to *D* band intensities between the samples with and without B, and the average size of graphene was estimated to be 1.2 nm.[3] The Raman spectra in Figure 1A also have shoulder peaks at around 1220 and 1440 cm^{-1} that are assignable to the symmetric vibrational mode of C–C bonds in finite domain size polycyclic aromatic hydrocarbons (PAHs).[7] This indicates that these *a*-C materials consist of a mixed structure of small carbon sheets and PAHs. Figure 1B shows XRD patterns of the prepared samples and broad diffraction peaks at $2\theta = 20$–30° that correspond to the (002) diffraction peaks for graphite,[8] which indicates that the materials are composed of aromatic carbon sheets oriented in a considerably random fashion.

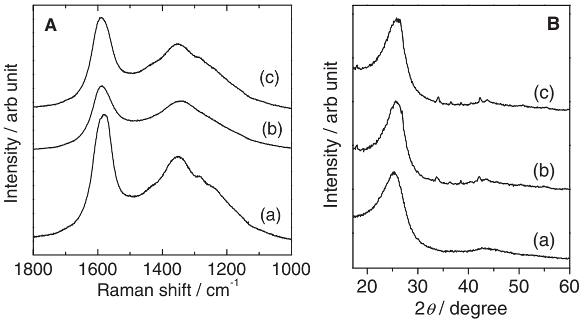

Figure 1. Raman spectra and XRD patterns of *a*-C doped with various B contents: (a) 0, (b) 0.5, and (c) 1.0 atom %.

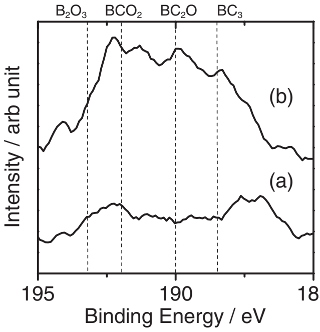

Figure 2. B1s XPS spectra of the *a*-C doped with different content of B (a) 0.5 and (b) 1.0 atom %.

X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma (ICP) analyses were used to investigate the electronic states and atomic concentrations of B in the B-doped *a*-C materials. Several B1s peaks appeared only in the XPS spectra for the B-doped *a*-C materials (Figure 2). Figure 2a shows the B1s XPS spectrum of the 0.5 atom % B-doped *a*-C material. A B1s peak due to B_2O_3 is observed at ca. 193 eV, which shows that part of the boron in the material is oxidized to B_2O_3 by exposure to air. In contrast, the peak at ca. 188.5 eV can be attributed to B–C bonding,[9] and the peaks at 190–192 eV are

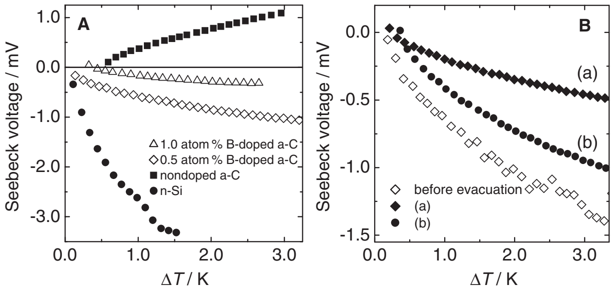

Figure 3. (A) Seebeck voltage as a function of temperature difference for various samples and (B) Seebeck voltage as a function of temperature for B-doped *a*-C before and after evacuation. (a) 0.5% B-doped sample heated at 573 K for 3 h under vacuum and (b) the same sample exposed to air for 3 weeks.

Table 1. Seebeck coefficient (S) and electrical conductivity (σ) of the samples[a]

Sample	$S/\mathrm{mV\,K^{-1}}$	$\sigma/\mathrm{S\,cm^{-1}}$
0.5 atom % B-doped *a*-C	-0.22	9.9×10^{-3}
1.0 atom % B-doped *a*-C	-0.12	4.8×10^{-4}
Nondoped *a*-C	0.069	8.4×10^{-2}
n-Si	-1.76	80.6

[a] Measurements carried out at 298 K.

assignable to oxidized boron species such as BC_2O and BCO_2.[10] The B/C atomic ratios of the 0.5 atom % B and 1.0 atom % B-doped *a*-C materials were estimated from the B1s to C1s peak intensity ratios to be 0.46 and 1.1%, respectively. These values are consistent with B contents estimated by ICP analysis. These results indicate that most of the introduced boron is successfully incorporated into *a*-C by the reaction of naphthalene and triphenylborane.

Semiconductivity of the samples was examined through Seebeck effect (Figure 3A).[11] The Seebeck effect is a thermoelectric effect: charge carriers move in response to a temperature gradient, resulting in Seebeck voltage. In the case of *a*-C without B, the Seebeck voltage increases with increasing ΔT. This indicates that *a*-C without B shows p-type semiconductivity as well as carbon-based semiconductors.[12,13] On the other hand, the correlation of the Seebeck voltage with ΔT for the B-doped samples has a negative slope. The Seebeck coefficient (S) and electric conductivity (σ) of each sample are summarized in Table 1. These results suggest that B-doped *a*-C functions as an n-type semiconductor; hence, electrons are the major carriers in B-doped *a*-C. It is well known that carbon materials become p-type semiconductors by replacement of the carbon atoms in the carbon framework with B atoms.[14,15] Therefore, the n-type semiconductivity of the B-doped samples cannot be attributed to B in the carbon hexagonal plane. Partially oxidized boron species such as BC_2O and BCO_2 bonded to the edges of the carbon sheets may contribute to the semiconductivity of the B-doped carbon materials. 0.5 atom % B-doped *a*-C has a larger Seebeck coefficient and higher electrical conductivity than 1.0 atom % B-doped *a*-C, as shown in Table 1. Defined bands due to PAHs are not observed in the Raman spectrum for the former sample but are for the latter sample (Figure 1A), which indicates that the addition of excess triphenylborane to naphthalene prevents carbonization. This may result in a decrease of the Seebeck coefficient and electrical conductivity of 1.0 atom % B-doped *a*-C.

It should be noted that the Seebeck coefficient of B-doped *a*-C is largely dependent on the atmosphere, as shown in Figure 3B. The results for 0.5 atom % B-doped *a*-C measured in air with moisture (298 K, humidity ca. 40–50%) shown in Figure 3B are the same as those of Figure 3A. The correlation of the Seebeck voltage with ΔT (298 K in air) for the sample after heating at 573 K for 3 h under vacuum is shown as (a) in Figure 3B, and the slope appears to be smaller than that before heat treatment. The Seebeck coefficient gradually increased with time and returned to that shown as (b) after 3 weeks. The Seebeck voltage–temperature difference curve of the sample returned to (a) after heating the sample in (b) at 573 K for 3 h under vacuum. Slow increase in the Seebeck coefficient at room temperature in air with moisture and decrease in the Seebeck coefficient after heat treatment under vacuum suggest that the reaction of boron species bonded to the carbon material with H_2O, rather than O_2, largely participates in the n-type semiconductivity of the material. The structure and characteristics of such boron species are currently under investigation.

In summary, B-doped *a*-C prepared from naphthalene and triphenylborane exhibits n-type semiconductivity. The semiconductivity can probably be attributed to H_2O adsorption on the carbon material, and further investigations are underway to confirm this.

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