Possible Charge-Ordered States in Boron–Nitride and Boron–Carbon–Nitride Nanotubes and Nanoribbons

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Electronic states in boron–nitride and boron–carbon–nitride nanoribbons with zigzag edges are studied using the extended Hubbard model with nearest-neighbor Coulomb interactions. Charge- and spin-polarized states are considered, and the phase diagram between two states is obtained. Next, electric capacitance is calculated to examine the nanofunctionalities of the system. Owing to the presence of strong site energies, the charge polarized state overcomes the spin polarized state, yielding a large difference in the phase diagram compared with that of a graphite system. Electronic structures are always like that of semiconductors. Capacitance is inversely proportional to ribbon width, owing to the presence of the charge excitation energy gap. [DOI: 10.1143/JJAP.45.7237]

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We will discuss that spin excitations tend to be suppressed owing to the presence of the large energy gap. This results in an enlarged region of the CP state in the phase diagrams of the BN and BCN systems. This property is markedly in contrast to the dominant SP state of the zigzag graphite ribbons.

The next topic of interest in this paper is how such electronic properties appear in measurable quantities. We consider electric capacitance because the CP state is accompanied by dielectric moment with respect to the charge orders. The “differential capacitance” is calculated as a response of the charge to the weak static field applied to the system in the transverse direction. The same method has been adopted in a recent study.10 We find that the calculated capacitance is inversely proportional to the distance between positive and negative electrodes. This behavior could be explained on the basis of the presence of an energy gap for charge excitations.

We will also consider the electronic properties of zigzag BCN nanoribbons, where $N$ and $L$ are the width and length of the ribbon, respectively. Fig. 1(a) shows the zigzag BN ribbons, and Fig. 1(b) shows the zigzag BCN ribbons. The periodic boundary condition is set along the $y$-axis parallel to the zigzag lines. Since the zigzag ribbon is a bipartite lattice, $A$ (boron) and $B$ (nitrogen) sites are denoted by filled and open circles in Fig. 1(a), respectively. All the twofold coordinated sites in the lower and upper zigzag edges belong to the $A$ and $B$ sites.

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$B$ sublattices, respectively, at which edge states are mainly localized. In Fig. 1(b), $B$ atoms are present along the upper zigzag edge sites, whereas $N$ atoms are present along the lower edges. The inner part is composed of $C$ atoms. The closed, shaded, and open circles denote $B$, $C$, and $N$ atoms, respectively. Experiments on the low concentration limit of $B$ and/or $N$ doping into carbon nanotubes have sometimes suggested the accumulation of impurity atoms at edge sites.8)

The formation of zigzag nanotubes is favored. Therefore, we choose this structure as a model system. We extend the model 4) with the site energy $E_N$ at the boron sites, and with $E_B$ at the nitrogen sites. To examine the nanofunctionalities as "nanosize condensers", the electric capacitance $C$ of the zigzag ribbons is determined by the method described in a previous study.10) The bond length is 1.45 Å.

First, we discuss the electronic properties of the zigzag BN nanotubes and nanoribbons. The lattice structure is shown in Fig. 1(a). The site energies at $B$ and $N$ are taken to be $E_B = +t$ and $E_N = -t$, respectively. The realistic magnitude $t$ ~ 2 eV gives the energy gap $2t$ ~ 4 eV reported in band calculations.8,9) Similar site energies in the single-orbital tight-binding model have been chosen for the random doping of BCN alloys in the literature.12) The total electron number is the same as the site number. This ensures the charge neutrality of the system.

Figure 2(a) shows a typical example of the charge density distribution of the CP state for the on-site interaction $U = \beta t$ and the nearest-neighbor repulsion $V = 0$ ($t$ is the hopping integral of electrons), and Fig. 2(b) shows the $z$-component of the spin density distribution of the SP state for $U = 4t$ and $V = 0$. The size of the zigzag ribbon is $4 \times 20$ sites. The filled and open circles denote positive and negative densities, respectively. Their radii are proportional to the magnitudes of the charge or spin densities: the maximum is 0.60 in Fig. 2(a) and 0.35 in Fig. 2(b). Owing to the strong site energies, there are alternations of electron number density, that extend over the system in Fig. 2(a). Furthermore, at the $B$ sites along the upper edge, positive charge density is enhanced compared with that at the inner part of the ribbon. At the $N$ sites along the lower edges, the negative density becomes similarly enhanced. As the interaction $U$ becomes stronger, the system changes into the SP state via phase transition. Figure 2(b) shows the spin density distributions. The alternations of spins are quite strong owing to the very large interaction parameter. The absolute values of spin density are enhanced along the two edges. Such modulations of the CP and SP near the edges are the result of the wavefunctions localized along the edge sites, as we have discussed for graphite ribbons.4)

The total energies of the CP and SP solutions are compared, and the phase diagram of the stable state is shown in Fig. 3. The calculation is performed for $N = 4$ and $L = 40$. The phase boundary, denoted by the bold line, indicates the first order phase transition. The dashed line is the strong correlation limit, $V = N(U + 2E_N)/(3N - 1) = 4(U - 2t)/11$, which can be obtained by considering the energies of the two states as being equal. The bold line approaches the dashed line, as $U$ and $V$ increase. The strong site energy difference gives rise to huge charge polarizations, as shown in Fig. 2(a). The region of the CP state extends in the phase diagram, and the SP state is highly suppressed. The realistic values of the interactions might be near the regions, $0 < U < 3t$ and $V \sim 0$, which correspond to CP states in the phase diagram. For the nanographite ribbon,4) the phase boundary crosses the origin $(U, V) = (0, 0)$. Thus, the SP state has been found in these regions. The strong site energies of the BN system have resulted in a marked change in ordered states between the graphite and BN systems.

Figure 4 shows the electric capacitance of the zigzag BN ribbons for $L = 20$ as a function of ribbon width. As the ribbon becomes wider, the system develops into a zigzag (10, 0) nanotube. The raw value of the capacitance $(a)$ and its inverse $(b)$ are plotted. We consider the three parameter sets of Coulomb interactions. The system is in the CP state for these parameters. All the curves indicate that capacitance is almost inversely proportional to ribbon width. There is a large electronic gap owing to the strong site energy difference. The system is intrinsically a semiconductor. The large charge excitation energy gap results in the inversely

![Fig. 2](image-url) Charge density distribution of CP state for $U = 1t$ and $V = 0$, and (b) $z$-component of spin density distribution of SP state for $U = 4t$ and $V = 0$, on zigzag BN ribbon with $4 \times 20$ sites. The filled and open circles denote positive and negative densities, respectively. Their radii are proportional to the magnitude of the charge or spin density: the maximum is 0.60 in (a) and 0.35 in (b).

![Fig. 3](image-url) Phase diagram on $U$–$V$ plane of zigzag BN ribbon with $4 \times 40$ sites. The bold line is the phase boundary, and the dashed line is the strong correlation limit.

![Fig. 4](image-url) Electric capacitance calculated for CP state of zigzag BN ribbons at $U = 0$, $1t$, and $2t$ for $V = 0$. The ribbon length is $L = 20$. The magnitudes of (a) capacitance and (b) its inverse are plotted against the ribbon width in the units of Å.
proportional behavior. Even though the present capacitance is the “differential capacitance”, the dependence on spacer width is similar to that of the classical parallel electrode condenser. Such an analogy is interesting in view of the fact that the spacer of the “nanocondenser” is made of the intrinsic insulator of the BN system.

Next, we report the electronic properties of the zigzag BCN nanotubes and nanoribbons, compared with those of the BN systems. The lattice structure of the BCN systems is shown in Fig. 1(b). In the present calculations, the site energies at B and N are taken to be $E_B = +0.8t$ and $E_N = -0.8t$. Because the system is mainly composed of carbon, we take $t \sim 2.5$ eV.

Figure 5(a) shows a typical example of the charge density distribution of the CP state for $U = 1t$ and $V = 0$, and Fig. 5(b) shows the $z$-component of the spin density distribution of the SP state for $U = 4t$ and $V = 0$. The maximum of the charge density is 0.41 in Fig. 5(a), and that of the spin density is 0.38 in Fig. 5(b). The polarization of charge is localized along the upper and lower edge sites in Fig. 5(a). It is extended over the system in Fig. 2(a). The change in the distribution patterns originates from the different types of atoms in the inner region of the nanoribbon. Figure 5(b) shows the spin density distributions of the SP state. The alternations of spins are quite strong, as we have found in Fig. 2(b). The spin polarization is less dependent on the site energy difference, in contrast to the charge polarization distribution. Similarly, the spatial enhancement in the CP and SP along the two edges is also obtained in Figs. 5(a) and 5(b). This is an effect due to the presence of the edge states.

Figure 6 shows the phase diagram between the CP and SP states, for the system with $N = 4$ and $L = 40$. The phase boundary indicates first-order phase transition. The dashed line, the strong correlation limit $V = (NU + EN)/(3N - 1) = (4U - 0.8t)/11$, approaches the bold line as $U$ and $V$ increase. We find the enhanced area of the CP state of the BN ribbon as shown in Fig. 3. The system also exhibited charge polarizations for the realistic values of the interactions. The decrease of the slope of the dashed lines between Figs. 3 and 6 is due to the decrease of the number in B and N atoms.

Finally, we analyze the electric capacitance of the BCN system. The calculations are performed for the system size $L = 20$, and the results are shown in Fig. 7. We consider the two parameter sets of Coulomb interactions. The system is in the CP state for these parameters. Again, we find that capacitance is almost inversely proportional to ribbon width.

In summary, the charge and spin polarized states have been discussed using the extended Hubbard model for BN and BCN nanotubes and ribbons. Next, electric capacitance has been calculated. Owing to the presence of the strong site energies, the CP state overcomes the SP state, yielding a large difference in the phase diagram in comparison with the calculations for the graphite system. The electronic structures of the BN and BCN systems are similar to that of semiconductors. Capacitance is inversely proportional to the distance between the positive and negative electrodes, owing to the presence of the charge excitation energy gap.

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