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# Thermal Properties of Carbon Doped Monolayer h-BN Systems: A Tight Binding Model Study

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**Abstract**: We report here a tight binding model study of hexagonal boron nitride (h-BN) 50% doped with carbon (C) atoms at the boron or nitrogen sublattice sites. The model Hamiltonian is written considering the effect of first, second and third nearest neighbor hopping interactions. The model Hamiltonian is solved using Zubarev's Green's function technique to find out the electron density of states. The temperature dependent entropy and specific heat for pure h-BN, h-BC and h-CN systems are computed and compared.

**Keywords:** Hexagonal boron-nitride; electron/hole doping; specific heat

## 1. Introduction

Following the same procedure as graphene separated from graphite, some new two-dimensional materials can be exfoliated from other layered materials. Among such new materials, there are several complex oxides, dichalcogenides and boron nitrides, which exhibit high crystal quality and macroscopic continuity [1]. Hexagonal boron nitride (h-BN) is emerging as a system which can be used as a platform for substrate of graphene or buffer layer between substrate and graphene in electronic devices, as the interaction between graphene and BN is very weak. The BN is an insulator with a band gap of ~5-7 eV. In comparison to graphene on $SiO_2$ substrate, graphene on hexagonal BN (h-BN) exhibits high electron mobility, low intrinsic doping and low carrier in-homogeneity. Apart from the above said applications, fabrication of large area (~ $cm^2$) h-BN layer opens the possibility of mass production of this new 2-D material. These properties of single layer h-BN has increased the interest of researchers in doing fundamental research on h-BN. The chemical [2] and mechanical [3]

experimental exfoliation of single layer h-BN has been done. Further, several experimental studies like optical and Raman spectroscopy [4], TEM characterization [2] have been done. Parallel theoretical studies on single and bi-layer h-BN also have been performed using density functional theory (DFT) [5,6] and tight binding (TB) model along with DFT [7,8]. All these studies confirm opening of band gap in h-BN.

In the present communication, we report a TB model study of single layer h-BN using Green's function technique. We consider the first, second and third nearest neighbor electron hoppings in the h-BN system. We observe opening of band gap through the study of electron density of states (DOS) and electron entropy and specific heat. We have compared the results for pure h-BN and 50% carbon doped h-BN at boron/nitrogen sites.

## 2. Formalism

The model Hamiltonian for the doped honeycomb lattice boron nitride system is written as

$$H = \sum_{k,\sigma}\left(\epsilon_B(k) a^{\dagger}_{k,\sigma} a_{k,\sigma} + \epsilon_N(k) b^{\dagger}_{k,\sigma} b_{k,\sigma}\right) + \sum_{k,\sigma}\left(\epsilon_{1,3}(k) a^{\dagger}_{k,\sigma} b_{k,\sigma} + \epsilon^{*}_{1,3}(k) b^{\dagger}_{k,\sigma} a_{k,\sigma}\right) \quad (1)$$

Here $\epsilon_{\alpha,k}(k) = -t_\alpha \gamma_\alpha(k)$, for $\alpha = 1-3$, is the electron band dispersion energy with $t_\alpha$ and $\gamma_\alpha(k)$ as the hopping integrals and Fourier transformed electron band dispersions in k-space for first, second and third nearest neighbor electron hoppings. The $\epsilon_B(k) = E_B + \epsilon_{2,k}$; $\epsilon_N(k) = E_N + \epsilon_{2,k}$ and $\epsilon_{1,3}(k) = \epsilon_{1,k} + \epsilon_{3,k}$ with $E_B$ and $E_N$ being the site energies of boron and nitrogen at sub-lattice sites respectively. The creation (annihilation) operators at boron and nitrogen sub-lattice sites are given by $a^{\dagger}_{k,\sigma}$ $(a_{k,\sigma})$ and $b^{\dagger}_{k,\sigma}(b_{k,\sigma})$ respectively. Above model Hamiltonian is solved using the equation of motion method of Zubarev's Green's function technique [9]. The two electron Green's functions at boron lattice site are calculated to be

$$G_{B1}(k,\omega) = \ll a_{k,\sigma}; a^{\dagger}_{k,\sigma} \gg_\omega = \frac{(\omega - \epsilon_N(k))}{2\pi|D(\omega)|};$$

$$G_{B2}(k,\omega) = \ll b_{k,\sigma}; a^{\dagger}_{k,\sigma} \gg_\omega = \frac{\epsilon^{*}_{1,3}(k)}{2\pi|D(\omega)|}$$

and the two electron Green's functions at nitrogen atom site are calculated as given below

$G_{N1}(k,\omega) = \ll b_{k,\sigma};\, b^{\dagger}_{k,\sigma} \gg_{\omega} = \frac{(\omega-\epsilon_B(k))}{2\pi|D(\omega)|}$ ;

$G_{N2}(k,\omega) = \ll a_{k,\sigma};\, b^{\dagger}_{k,\sigma} \gg_{\omega} = \frac{\epsilon_{1,3}(k)}{2\pi|D(\omega)|}$

where $|D(\omega)| = (\omega - \epsilon_B(k))(\omega - \epsilon_N(k)) - |\epsilon_{1,3}(k)|^2$ and the two quasi-particle band energies are obtained as

$$\omega_{s,k} = E_0 + \epsilon_{2,k} - (-1)^s \frac{1}{2}\sqrt{E_g^2 + 4|\epsilon_{1,3}(k)|^2} \qquad (2)$$

Here $s = 1$ represents the upper conduction band and $s = 2$ represents the lower valence band, $E_0 = \frac{1}{2}[E_B + E_N]$ and the band gap $E_g = E_B - E_N$ at Dirac point. The momentum dependent gap between conduction band and valence band is $\Delta = \omega_{1,k} - \omega_{2,k} = \sqrt{E_g^2 + 4|\epsilon_{1,3}(k)|^2}$. For pristine h-BN the site energies at boron and nitrogen sites are $E_B = 2.46$ eV and $E_N = -2.55$ eV respectively [10]. The hopping parameters are $t_1 = -2.16$ eV, $t_2 = -0.04$ eV and $t_3 = -0.08$ eV. These quantities in dimensionless form appear as $e_b = {}^{E_B}/_{t_1} = 1.139$, $e_n = {}^{E_N}/_{t_1} = 1.180$, $\tilde{t}_1 = {}^{t_1}/_{t_1} = 1.0$, $\tilde{t}_2 = {}^{t_2}/_{t_1} = 0.0185$ and $\tilde{t}_3 = {}^{t_3}/_{t_1} = 0.037$, $c = {}^{\omega}/_{t_1}$ .

## 3. Results and Discussion

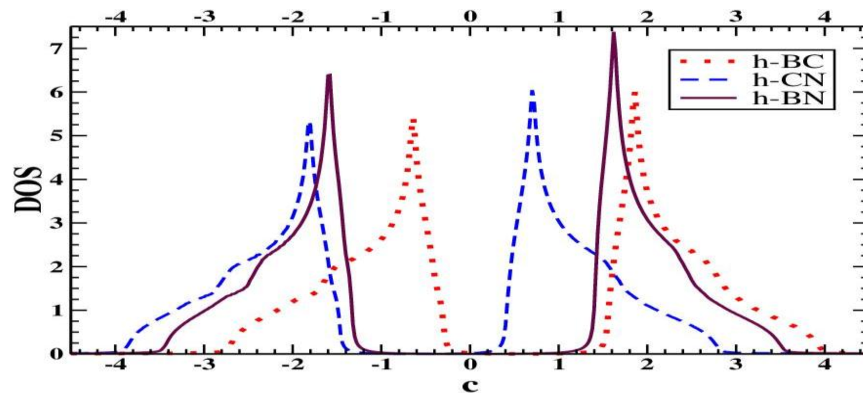
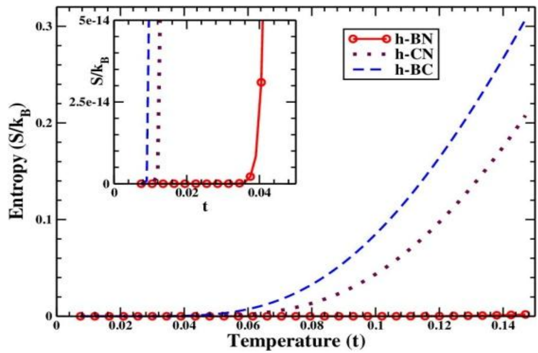



**Figure 1:** The energy dependent electron DOS for h-BC, h-CN and h-BN systems

Boron and nitrogen site Green's functions ($G_{B1}(k,\omega)$, $G_{N1}(k,\omega)$) are calculated by Zubarev's Green's function technique. The electron density of states (DOS), which is proportional to the tunneling conductance of h-BN is calculated from the imaginary part of these Green's functions. The DOS is computed by taking 1000x1000 grid points of electron momentum in monolayer h-BN plane as shown in figure 1. The band energy dependent DOS of monolayer h-BN exhibits a band gap of energy $\Delta_{BN}/t_1 \simeq \sim 2.4$ ($\Delta_{BN} \simeq 2.4 \times 2.16 = 5.184$eV) around Dirac point at energy $c = 0$ lying between two sharp peaks appearing at van Hove singularity indicating that h-BN is a very good insulator. The 50% doped monolayer h-BN with carbon atoms at boron sites forms the system h-CN which shows a band gap of magnitude $\Delta_{CN}/t_1 \simeq 1.4$ ($\Delta_{CN} \simeq 3.0$eV) lying just below the Dirac point ($c = 0$) indicating the electronegative character of h-CN system. Similarly, the 50% doped monolayer h-BN with carbon atoms at nitrogen sites forms h-BC system which shows a band gap of $\Delta_{BC}/t_1 \simeq 1.2$ ($\Delta_{BC} \simeq 2.59$eV) lying just above the Dirac point indicating the electropositive character of h-BC system. Thus we conclude that the 50% boron/nitrogen site carbon doped h-BN system exhibits much reduced band gap near the Dirac point exhibiting semiconducting property of the system. The pristine h-BN systems with a suitable concentration of carbon doping can produce a band gap ~ 1 eV and the system can be used as an ideal semiconductor applicable for semiconductor devices.



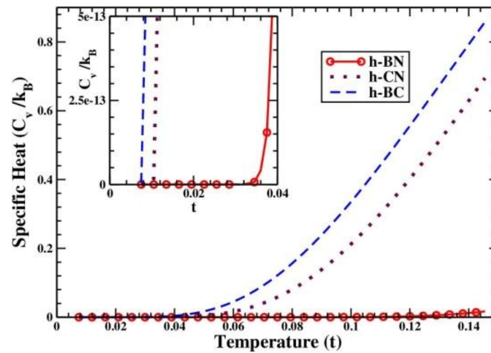




**Figure 2** **Figure 3**

**Figure 2:** The temperature dependent electron entropy for h-BN, h-CN and h-BC systems.

**Figure 3:** The temperature dependent electron specific heat for h-BN, h-CN and h-BC systems.

The electronic free energy of the monolayer h-BN and its doped systems is written in terms of the band energies. The temperature dependent entropy (S) and electron specific heat $C_v$ are calculated from the free energy using the formulae $S = -\left(\frac{\partial F}{\partial T}\right)_{\mu,v}$ and $C_v = T\left(\frac{\partial S}{\partial T}\right)$ as shown in figures 2 and 3. The figure 2 shows the temperature dependent entropy $\left(\frac{S}{k_B}\right)$ for the systems h-BN, h-CN and h-BC. It is observed that the entropies at a given temperature for doped systems are higher than the pure h-BN systems due to their reduced band gap near the Dirac point i.e. the band gaps are $\Delta_{BN} \approx 5.184$ eV, $\Delta_{CN} \approx 3.0$ eV and $\Delta_{BC} \approx 2.59$ eV as calculated from the DOS given in figure 1. The entropy becomes zero at low temperatures and it increases with increase of temperature. The magnified plot of $s/k_B$ is shown in the inset of figure 2. The entropy is zero for h-BC system for temperatures t<0.008 (T = 0.008x2.16x10000 = 172.8 K), for h-CN system for t < 0.01 (T < 216 K) and for h-BN system for t < 0.032 (T < 691.2 K).

Figure 3 shows the temperature dependent electron specific heat of pure monolayer h-BN and its doped counterparts. It is observed that the specific heats of doped systems at a given temperature are larger compared to the pure h-BN system due to their decreasing order of band gaps near the Dirac point. The electron specific heat of 50% doped system h-BC at a given temperature having a lower band gap ($\Delta_{BC} \approx 2.59$ eV) is the highest among the three systems. It is observed that the electron specific heat at lower temperatures become zero and then increases with the increase of temperature. The magnified plot of $C_v/k_B$ at lower temperatures is shown in the inset of figure 3. The specific heats are zero for h-BC system for temperatures t < 0.008, for h-CN system for t < 0.01 and for h-BN system for t < 0.032 indicating the absence of electron densities at low temperatures.

## 4. Conclusion

From our present tight binding model calculations of the electron DOS, electron entropy and electron specific heat, we conclude that the carbon doped h-BN system can be a good candidate for the synthesis of semiconducting materials having the potential of its application in nano-electronic devices.

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