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Criticality of Surface Topology for Charge-carrier Transport Characteristics in Two-Dimensional Borocarbonitrides: Design Principle of an Efficient Electronic Material

Swastika Banerjee,^{a,b}and Swapan K. Pati^{*a,b,c} ^aNew Chemistry Unit, ^bJawaharlal Nehru Center for Advanced Scientific Research, Bangalore 560064, India ^cTheoretical Sciences Unit E-mail: <u>swapan.jnc@gmail.com</u>

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METHODS

In the DFT calculations, we use projector augmented wave (PAW) method ¹ for representation of ionic core and valence electrons. The exchange-correlation energy of electron is described by the functional of Perdew, Burke, and Ernzerhof (PBE). ² We use an energy cutoff of 500 eV for truncation of plane wave basis. The Brillouin zone was represented by Monkhorst–Pack special k-point mesh of $30 \times 30 \times 1$. Large enough supercell has been considered to ensure that the vacuum space is 20 Å assuring sufficient vacuum along non-periodic direction. Optimized lattice vectors appear to be 8.72 (x); 7.56 (y) for BCN-I-AB unit cell and 13.05(x); 7.54(y) for BCN-II-AB unit cell (see Fig 2). GPW formalism and GTH pseudo-potential ³ with Perdew–Burke–Ernzerhof (PBE) ² exchange correlation functional have been used for AIMD simulation, adopting the CP2K set of programs. ^{4,5}

In principle, different scattering channels can be added in the following way:

$$\frac{1}{\tau} = \frac{1}{\tau_{optical}} + \frac{1}{\tau_{acoustial}} + \frac{1}{\tau_{impurity}}$$
(3)

Where, the subscripts denote acoustic, optical phonons, and impurity respectively. Here, only the acoustic phonon scattering has been considered. In the carrier transport calculation, we have a periodic super cell representation along two directions x and y for 2D sheet. The Deformation Potential constant is defined as $E^{\beta_1} = \Delta E / (\Delta l/l_0)$, where ΔE is energy shift of the band edge position with respect to the lattice

dilation $\Delta l/l_0$ along the direction (β) of the external field. The total energy (*E*) of a unit cell as a function of lattice dilation ($\Delta l/l_0$) obey the relation ($E - E_0$)/ $S_0 = C^{\beta} (\Delta l/l_0)^2/2$. We thus evaluate the elastic constant (C^{β}) of the sheet along the transport direction β . Here S_0 and E_0 are the area and total energy of the optimized super cell structure. Δl is the deformation of lattice constant along the direction (β) and l_0 is its value at equilibrium geometry, a_0 or b_0 .



Fig. S1.a (C) Unequal separations (three and five atoms) between localized C-domains and (D) long bridging chain (seven atoms) between two localized C-domains.

Table T1. Deformation Potential E_1 , Elastic Constant C^{β} , Carrier Mobility μ , and the Averaged Value of Scattering Relaxation Time τ at 300 K for electrons and holes in monolayer C, D (B_{2.5}CN_{2.5}) (shown in Fig. S1) and E, F surface topologies (shown in Fig. 2 in main text).

Sheet	Carrier type	E_1 (eV)	C^{β} (J/m2)	μ (cm2/V s)	τ(ps)
С	ex	3.52	304.18	0.07	0.51
	h ^x	0.66	304.18	5.07	18.54
	e ^y	3.96	301.77	0.05	0.40
	h ^y	1.76	301.77	0.71	2.59
D	e ^x	2.20	308.20	0.16	9.01
	h ^x	2.20	308.20	0.22	9.29
	e ^y	4.62	302.61	0.04	2.01
	h ^y	0.44	302.61	5.41	150
Е	e ^x	2.64	308.20	3.09	3.51
	hx	2.64	308.20	3.06	2.44
	e ^y	3.52	308.56	1.75	1.98
	hy	0.22	308.56	441.42	352.23
F	e ^x	1.32	345.66	31.15	33.52
	hx	3.08	345.66	5.7	6.16
	e ^y	3.96	336.06	3.37	3.62
	h ^y	1.10	336.06	43.61	46.93

For Both BCN-I and BCN-II, AA stacking pattern shows least band gap whereas AB stacking or other turbulent stacking patterns are energetically more stable with little more opening of band-gap. Tuneability of band structure and lifting of the degeneracy in conduction and valence band is also found through change in the stacking pattern in case of BCN-II type. Whatever the stacking it is, electronic band gap for BCN-II is pretty larger in comparison with BCN-I. Band dispersion in BCN-I arises from the contributions of B, N and C to the valence band and mostly N 2pz orbitals to the conduction band (see Fig 4). On the other hand, localized C domain (BCN-II) introduces sharp localized peak (contributed by carbon 2pz orbitals) in the vicinity of the conduction band minimum (CBM). Hence the conduction bands are more flattened in BCN-II, which results in higher electronic effective mass whereas, C-valence 2pz orbital contribute to the broad peak near Valence Band Maximum (VBM).



Fig. S2. Band structure for (a) monolayer BCN-I and BCN-II; (b) bilayer BCN-I (c) bilayer BCN-II borocarbonitride ($B_{2.5}CN_{2.5}$) sheet in their various stacking pattern are obtained from DFT calculations. All of them exhibit direct band gap.



Fig. S3. Projected density-of-states of states for out-of-plane valence orbitals in bilayer borocarbonitride ($B_{2.5}CN_{2.5}$) sheet (BCN-I in the left and BCN-II in the right) in their stable stacking pattern are obtained from DFT calculations.

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