Tunable band gap of boron nitride interfaces under uniaxial pressure

2012 J. Phys.: Condens. Matter 24 475502

(http://iopscience.iop.org/0953-8984/24/47/475502)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **24** (2012) 475502 (4pp) doi:10.1088/0953-8984/24/47/475502

Tunable band gap of boron nitride interfaces under uniaxial pressure

Elizane E Moraes, Taíse M Manhabosco, Alan B de Oliveira and Ronaldo J C Batista

Departamento de Física, Universidade Federal de Ouro Preto, Ouro Preto, MG, 35400-000, Brazil

E-mail: oliveira@iceb.ufop.br

Received 4 September 2012, in final form 5 October 2012
Published 26 October 2012

Abstract

In this work we show, by means of a density functional theory formalism, that the interaction between hydrogen terminated boron nitride surfaces gives rise to a metallic interface with free carriers of opposite sign at each surface. A band gap can be induced by decreasing the surface separation. The size of the band gap changes continuously from zero up to 4.4 eV with decreasing separation, which is understood in terms of the interaction between surface states. Due to the high thermal conductivity of cubic boron nitride and the coupling between band gap and applied pressure, such tunable band gap interfaces may be used in highly stable electronic and electromechanical devices. In addition, the spatial separation of charge carriers at the interface may lead to photovoltaic applications.

(Some figures may appear in colour only in the online journal)

Diamond is commonly used as an abrasive material in technological and industrial applications due to its hardness. Other intrinsic properties of diamond have increased its range of applications from biotechnology to electronics [1–4]. In electronics, in particular, its large electronic band gap and exceptionally high thermal conductivity led to the production of highly stable solid state transistors (FETs) based on hydrogen terminated diamond [3–5]. Due to the similarity between the isoelectronic C–C and B–N bonds, boron and nitrogen form a material analogous to the carbon diamond, namely, cubic boron nitride (cBN). cBN presents hardness, band gap, and thermal conductivity very similar to those of carbon diamond. In addition, it is also possible to produce hydrogen terminated cBN [6] surfaces. Nevertheless, the C–H is not isoelectronic to B–H and N–H bonds, thus hydrogen terminated diamond and hydrogen terminated cBN must present distinct electronic and electrochemical properties. For example, the band gap of thin hydrogen terminated cBN films depends on the number of BN layers due to the differences between B–H and N–H terminated surfaces [7]. On the other hand, the band gap of thin diamond films is constant.

In this work, we apply a density functional formalism to investigate interfaces formed by the interaction between hydrogen terminated boron nitride surfaces. We found that those interfaces present a band gap that can be continuously controlled by applied uniaxial pressure, which is explained in terms of the interaction between surface states due to the B–H and N–H terminations. The gap of the system can be modified from zero up to roughly 4.4 eV (a value of band gap close to that calculated for cBN within the density functional theory approach). Depending on the surface separation, the interface presents a metallic behavior with electrons at the N–H terminated surface and holes at the B–H terminated surface. The semiconductor, metallic, and insulating behavior of such interfaces may allow their use in electronics as highly stable devices. The coupling between applied pressure and the band gap, on the other hand, may permit the use of such interfaces in electromechanical devices. Besides, since the free carriers are spatially separated in those interfaces and the cBN is transparent for visible light, they could be also used in photovoltaic applications.

The applied first-principles methodology is based on the density functional theory (DFT) as implemented in the SIESTA program [8]. We used the generalized gradient approximation (GGA) as parametrized in the Perdew–Burke–Ernzerhof scheme (PBE) [9] for the exchange–correlation functional. The ionic core potentials were represented by norm-conserving scalar relativistic Troullier–Martins [10] pseudopotentials in Kleinman–Bylander nonlocal form [11]. The fineness of the real-space grid integration was defined by a minimal energy cutoff of 150 Ryd [12]. The geometries were fully optimized using

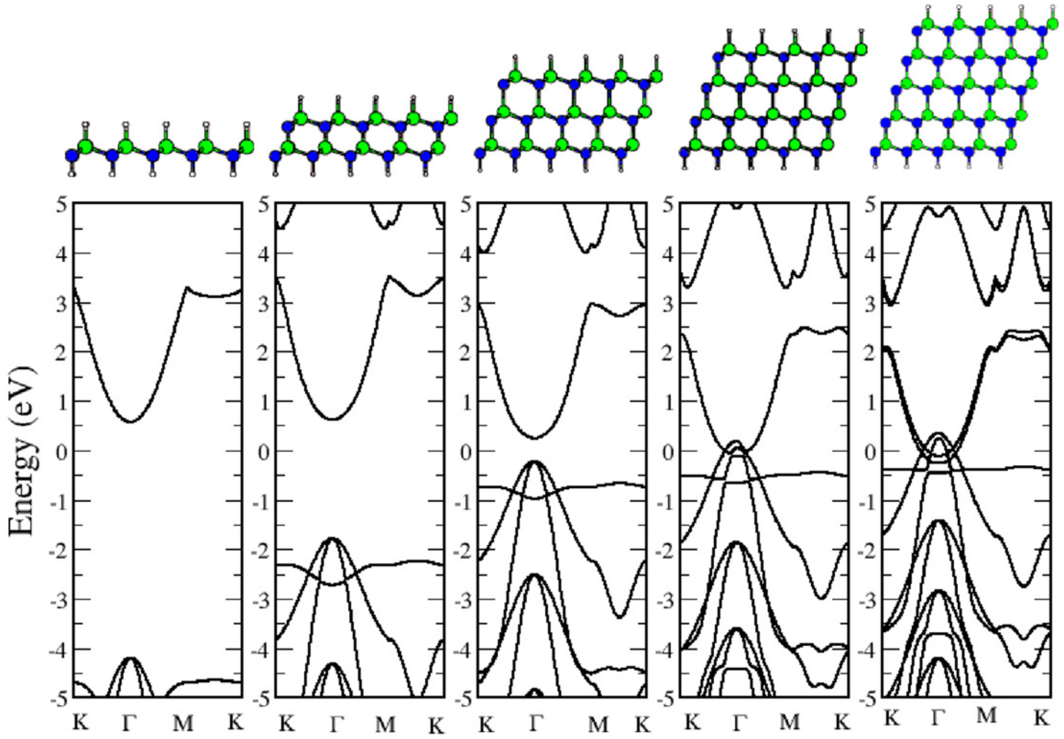

Figure 1. Bands structure of thin boron nitride nanofilms. From left to right the number of layers increases from one up to five. As the number of layers decreases the overlap between orbitals of atoms at each surface increases giving rise to band gaps.

the conjugate gradient algorithm [13] until all the force components were smaller than 0.02 eV Å^{-1}. The Kohn–Sham (KS) eigenfunctions were expanded as linear combinations of pseudo-atomic orbitals of finite range consisting of double-zeta radial functions per angular momentum plus polarization orbitals (DZP).

As a first step to understand the electronic properties of cBN interfaces we investigated few-layered hydrogenated (111) BN films. The top panels of figure 1 show the geometries of the few-layered films whose number of layers changes from one up to five while the bottom panels show the respective electronic structure. It is clear that there is a dependence of the band gap on the number of layers, which can be understood in terms of differences between B–H and N–H sp^3 terminations.

The C–C sp^3 bonds in diamond share a pair of electrons (satisfying then the octet rule) which leads to a wide band gap between valence and conducting states. Since boron and nitrogen are, respectively, the left and right neighbors of carbon in the periodic table of elements the B–N bond is isoelectronic to the C–C bond. Therefore, the B–N sp^3 bonds in cBN also share a pair of electrons where the excess of electrons of nitrogen orbitals are precisely offset by the lack of electrons in boron orbitals. As a result, cBN presents a band gap as wide as that of carbon diamond. In the N–H and B–H bonds on hydrogen terminated cBN, on the other hand, the H atoms do not compensate the excess or lack of electrons on N and B orbitals in cBN surfaces, which results in surface states within the large band gap of cBN. In a sufficiently thick film, the interaction between those surfaces is negligible. This is the case for films with four layers or more, in which there is no overlap between N–H and B–H orbitals (indeed, the distance between N and B atoms at both ends in the four-layer BN film is 7.12 Å, that is greater than twice the cutoff radius of N and B orbitals, 2.5 Å). In those cases, the edge of the occupied surface state localized at the B–H end is above the edge of the unoccupied surface state localized at the N–H end (the fourth and fifth panels of figure 1 show a superposition of non-interacting surface states). Thus, the N–H terminated surface can transfer charge to the B–H terminated surface if an interaction between surfaces is provided. In a very recent work [14], we have investigated by means of theory and experiment a similar case in which the interaction between semiconducting carbon nanotubes (SCNTs) and diamond surfaces—which are large gap insulators—allows a metallic response. In that case, the top of the valence band of the diamond surface was above the bottom of the conduction band of the SCNTs.

An interaction between the N–H and B–H terminated surface occurs in films with fewer than three layers since there is an overlap between orbitals of B and N atoms at different surfaces. In a single layer film (left panel of figure 1) the overlap between N and B orbitals is maximum, then the excess or lack of electrons at N–H and B–H surfaces is canceled out. As a result, the one layer cBN film presents a band gap very similar to that of cBN bulk. The overlap between orbitals of the atoms at different surfaces decreases with film thickness which leads to the values of band gap shown in the second and third panels of figure 1.

The results discussed above strongly suggest that the overlap between orbitals of the atoms of B–H and N–H

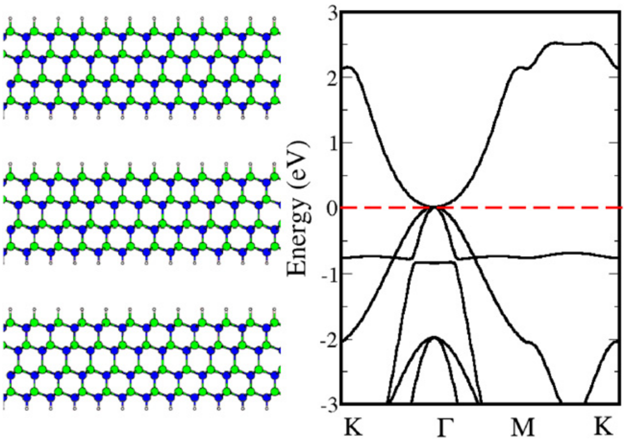

Figure 2. Left panel: interfaces formed by the physical contact between N–H and B–H terminated cBN four-layered films, only the first neighbors' periodical images are shown. The periodical images are vertically separated by 6.7 Å, which corresponds to roughly twice the cutoff radius of H s orbitals. Right panel: band structure of the interfaces shown in the left panel.

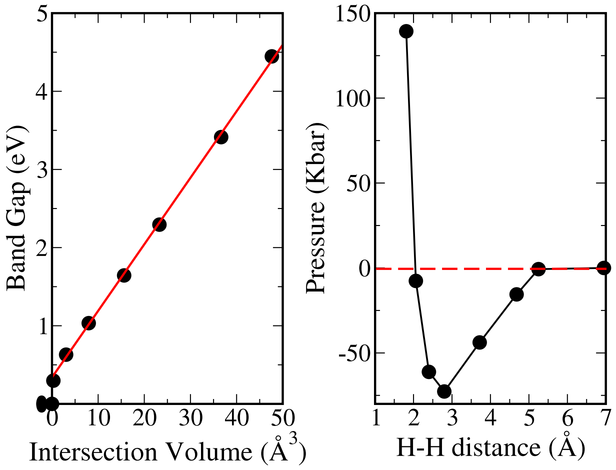

Figure 3. Left panel: band gap as a function of the intersection volume (see footnote 1) between hydrogen s orbitals of H atoms at the interface formed by the interaction between B–H and N–H terminated cubic boron nitride films with four layers, see left panel of figure 2. Right panel: uniaxial pressure as a function of the distance between hydrogen atoms at the B–H terminated surface and N–H terminated surface. Due to the finite range of the employed basis set, an abrupt jump in the band gap is observed in the left panel. See text for details.

cBN surfaces determine the band gap since it affects charge distribution that gives rise to the surface states. The overlap between the orbitals of atoms at different surfaces can be continuously controlled by the separation between surfaces, as shown in the left panel of figure 2. We have simulated the interaction between B–H and N–H terminated cBN surfaces by performing calculations on four-layer cBN nanofilms in which the distance between successive periodical images is keep fixed. The right panel of figure 2 shows the band structure of an interface formed by stacking a H terminated cBN surface onto its counterpart. It is possible to see that the band structure of such an interface differs from the band structure of an isolated four-layer film (fourth panel of figure 1). Such a difference is due to a charge transfer between the B–H and N–H surfaces that changes the position of surface states. In spite of that, the net charge transferred is not enough to open a band gap in the interface. Then, the N–H/B–H interface can be metallic, depending on the surface separation, with free charge carriers of opposite sign at each surface. The positive charge will, therefore, attract the negative charge at the adjacent surface, thereby producing a bidimensional electron gas. The combination of bidimensional electron and hole gases, very close to each other, could lead to interesting transport properties.

A decrease in the distance between B–H and N–H surfaces at the interface increases the overlap between orbitals of atoms at the surfaces. The left panel of figure 3 shows the band gap of the interface as a function of the sphere–sphere intersection volume between two identical spheres centered at H atoms[1]. It is possible to see that a precise linear dependence of the band gap on the intersection, which corroborates the importance of overlap between orbitals of atoms at surface for the band gap of few-layered films. Thus, any value of band gap ranging from zero up to 4.4 eV in the interface formed by the interaction between B–H and N–H cBN surfaces can be tuned through the uniaxial applied pressure. The right panel of figure 3 shows the values of uniaxial pressure as a function of the H–H distance. It is possible to see that the equilibrium distance between two surfaces corresponds to a H–H distance of 2.02 Å. Since we have considered a stacking configuration in which H atoms of one surface are placed between three H atoms of the other surface, the vertical equilibrium distance between surfaces is 1.38 Å. The abrupt transition seen in figure 3 (close to the origin) is due to the finite range of the localized basis set employed in this work. The numerical atomic orbitals used are solutions of the Kohn–Sham Hamiltonian for the isolated pseudo-atom. A strict localization of the basis function is ensured by adding a confining potential. Such a confining potential ensures that the matrix elements between two orbitals are zero if there is no overlap between them.

In summary, we report first-principles calculations on a tunable band gap interface composed of a highly stable material, cubic boron nitride. Such a result can be very interesting for industrial applications since: (i) highly stable tunable semiconductors are highly desired for electronics; (ii) the continuous dependence of the band gap on the applied pressure may be useful in very accurate electromechanical devices; (iii) the spatial separation of the charge carriers of opposite sign at the interface combined with the transparency of cBN bulk for visible light may allow the production of photovoltaic devices. The mechanism which leads to the dependence of the band gap with applied pressure is understood in terms of the interaction between surface states.

---

[1] The intersection volume common to the two spheres can be found by adding the volume of two spherical caps. The volume of a spherical cap of height h of a sphere of radius R is: $V(R,h) = \frac{\pi h^2(3R-h)}{3}$. For identical spheres $h = R - d/2$, where d is the distance between centers. Thus, the intersection volume is $2V(R,h) = \frac{\pi}{12}(4R+d)(2R-d)^2$.

Acknowledgments

The authors acknowledge financial support from CNPq, FAPEMIG, Rede Nacional de Pesquisa em Nanotubos de Carbono, and INCT-Nano-Carbono.

References

[1] Manhabosco T M and Müller I L 2009 *Appl. Surf. Sci.* **255** 4082–6
[2] Manhabosco T M and Müller I L 2009 *Tribol. Lett.* **33** 193–7
[3] Denisenko A and Kohn E 2005 *Diamond Relat. Mater.* **14** 491–8
[4] Moran D A J, Fox O J L, McLelland H, Russell S and May P W 2011 *IEEE Electron Device Lett.* **32** 599–601
[5] Taniuchi H, Umezawa H, Arima T, Tachiki M and Kawarada H 2001 *IEEE Electron Device Lett.* **22** 390–2
[6] Reinke P, Oelhafen P, Feldermann H, Ronning C and Hofsäss 2000 *J. Appl. Phys.* **88** 5597–604
[7] Zhang Z and Guo W 2012 *Nano Lett.* **12** 3650–5
[8] Soler J M, Artacho E, Gale J D, Garcia A, Junquera J, Ordejón P and Sánchez-Portal D 2002 *J. Phys.: Condens. Matter* **14** 2745–79
[9] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865–8
[10] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993–2006
[11] Kleinman L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425–8
[12] Moreno J and Soler J M 1992 *Phys. Rev.* B **45** 13891–8
[13] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos 1992 *Rev. Mod. Phys.* **64** 1045–97
[14] Barboza A M, Carara S S, Batista R J C, Chacham H and Neves B R A 2012 *Small* **8** 220